USSR/Chemistry - Physical Chemistry

Card : 1/1

Authors : Krylov, O. V., Memb. Corres. of Acad. of Sc. USSR., Roginskiy, S. Z. and Fokina, E. A.

Title : Investigation of the absorption method characterizing the alkaline properties of oxide catalysts

Periodical : Dokl. AN SSSR, 96, Ed. 6, 1183 - 1186, June 1954

Abstract : In order to investigate the catalytic properties of surfaces, acting according to the acid-basic mechanism, one must have proper methods of determining the number and quality of the acid and alkaline centers of the surface. The most effective methods are those based on the measurement of the value and stability of specific absorptions for such weak bases as: ammonia, pyridine, quinoline, and the methods based on the study of the poisoning effect of alkalis on the activity of catalysts. Twelve references. Graphs.

Institution : ...

Submitted : March 12, 1954

AF701597 TREASURE ISLAND BOOK REVIEW AID 842 - S

KRYLOV, O. V. and YE. A. FOKINA (Institute of Physical Chemistry, Academy of Sciences, USSR).
OB IZMERENII KISLOTNO-SHCHELOCHNYKH SVOYSTV POVERKHNOSTI (Determination of oxidation-reduction properties of surfaces).
In Problemy kinetiki i kataliza (Problems of Kinetics and Catalysis), vol. 8. Izdatel'stvo Akademii Nauk SSSR, 1955.
Section V: New experimental methods. p. 248-255.

The adsorption of phenol was studied in order to develop a method for the determination of the number and nature of acid and alkaline centers on the surface. It was determined gravimetrically on a quartz spring balance connected with an ampule containing phenol. The adsorption of phenol was conducted at 23-25°C; desorption, at 25, 100, 200, 300 and 380°C; adsorption at 100°C, desorption at 100, 200, 300 and 380° C; adsorption at 200°C, desorption at 200, 300 and 380°C. A study of the kinetics of adsorption and desorption of phenol was carried out on acidic, alkaline and amphoteric adsorbents. BeO, MgO, ZnO, CdO, CaO, Ca $(OH)_2$, Al_2O_3, silica gel, and the aluminosilicate cracking catalyst. The catalytic activity of the above catalysts were also studied in the decomposition of isopropyl alcohol. The experimental

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data are compiled in Table 1 (p. 250). The adsorption of phenol by all the catalysts except SiO_2 and Al_2O_3-SiO_2, is very stable (chemisorption).

The curve in Fig. 1 (p. 251) shows the quasi-isobars of adsorption (calculated from the saturation points of the kinetic adsorption isotherms). The amount of phenol adsorbed at 25°C on $1m^2$ catalytic surface is approximately the same (5-8mm) on different catalysts while the stability of the bond between phenol and catalyst differs for different catalysts. Data on the desorption of phenol from BeO and MgO at various temperatures are compiled in Table 2 (p. 252).

Kinetic isotherms of adsorption of phenol on BeO are shown in Fig. 2,(p. 253). Analogous isotherms were found for ZnO, MgO, Al_2O_3, etc., with the exception of CaO, $Ca(OH)_2$, silica gel and aluminosilicate. Kinetic isotherms of adsorption of phenol on aluminosilicate at various temperatures are shown in Fig. 3 (p. 253).

KRYLOV, O. V. and YE. A. FOKINA AID 842 - S

To establish the acidic nature of the catalytic surface, adsorption of pyridine was conducted in the same manner as the adsorption of phenol. The experimental data are compiled in table 3,(p. 254). Study of the decomposition of isopropyl alcohol showed that the dehydration ability of the catalyst changes as in the adsorption of pyridine, and the dehydrogenation ability of the catalyst as in the adsorption of phenol.

The adsorption of phenol can be used for quantitative determination of the basic nature of the surface. Other volatile substances with low acidity may be used.

Adsorption of pyridine may be used for determination of the acidic properties of the surface. It is advisable to determine also the heat of adsorption and the energy of activation. A similar method may be used for determination of the electronic nature of the catalytic surface.

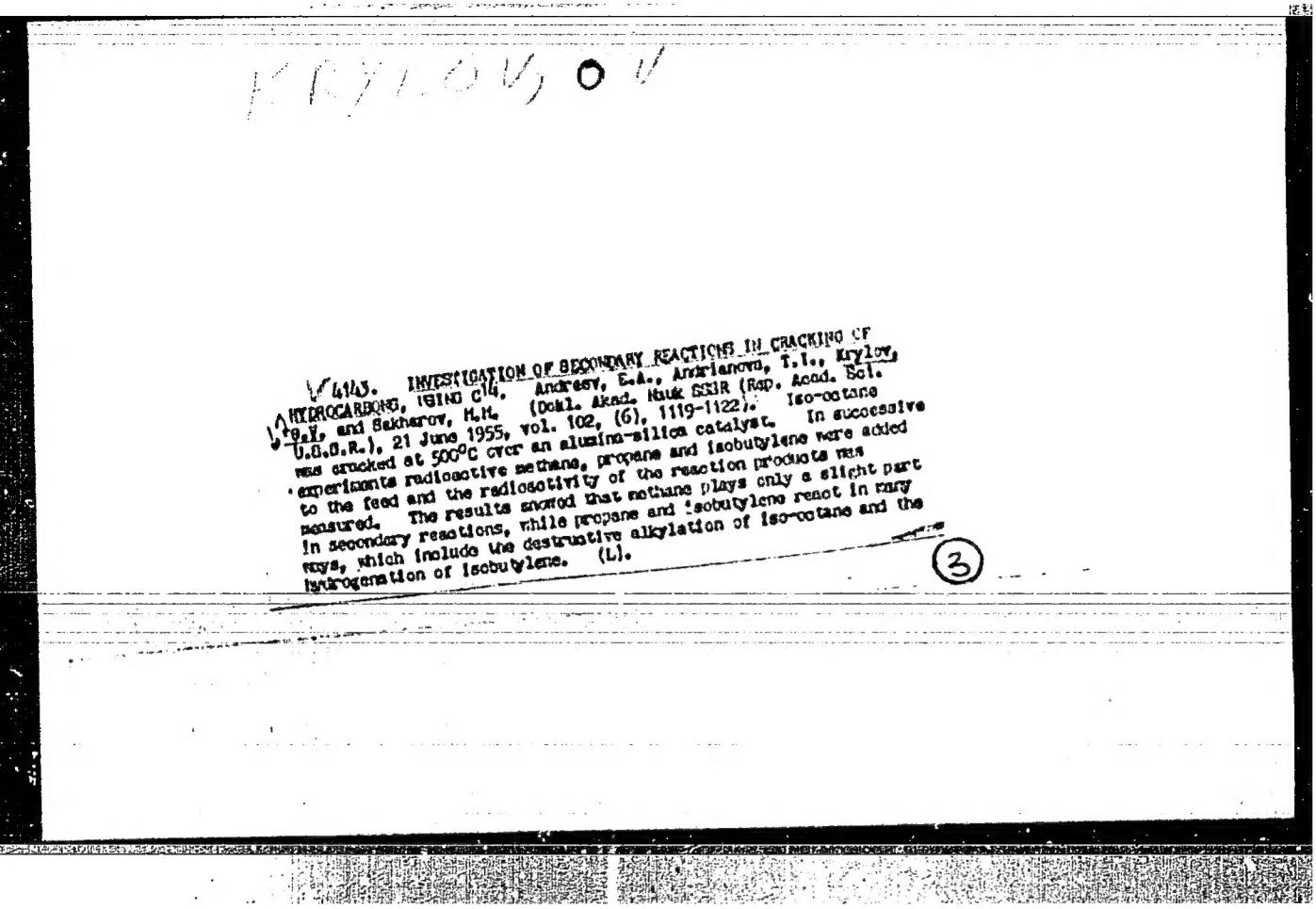
The effect of the adsorption of mercury, an electron-donor, and oxygen, an electron-acceptor on the catalytic nature of

KRYLOV, O. V. and YE. A. FOKINA AID 842 - S

oxides of Be, Zn and Cd was studied. Mercury and oxygen were supplied to the catalyst simultaneously with the vapors of isopropyl alcohol. Oxygen decreases the rate of decomposition of half of the initial value - see ref. 19. Three tables, 3 diagrams. 19 references, 12 Russian (1946-1954).

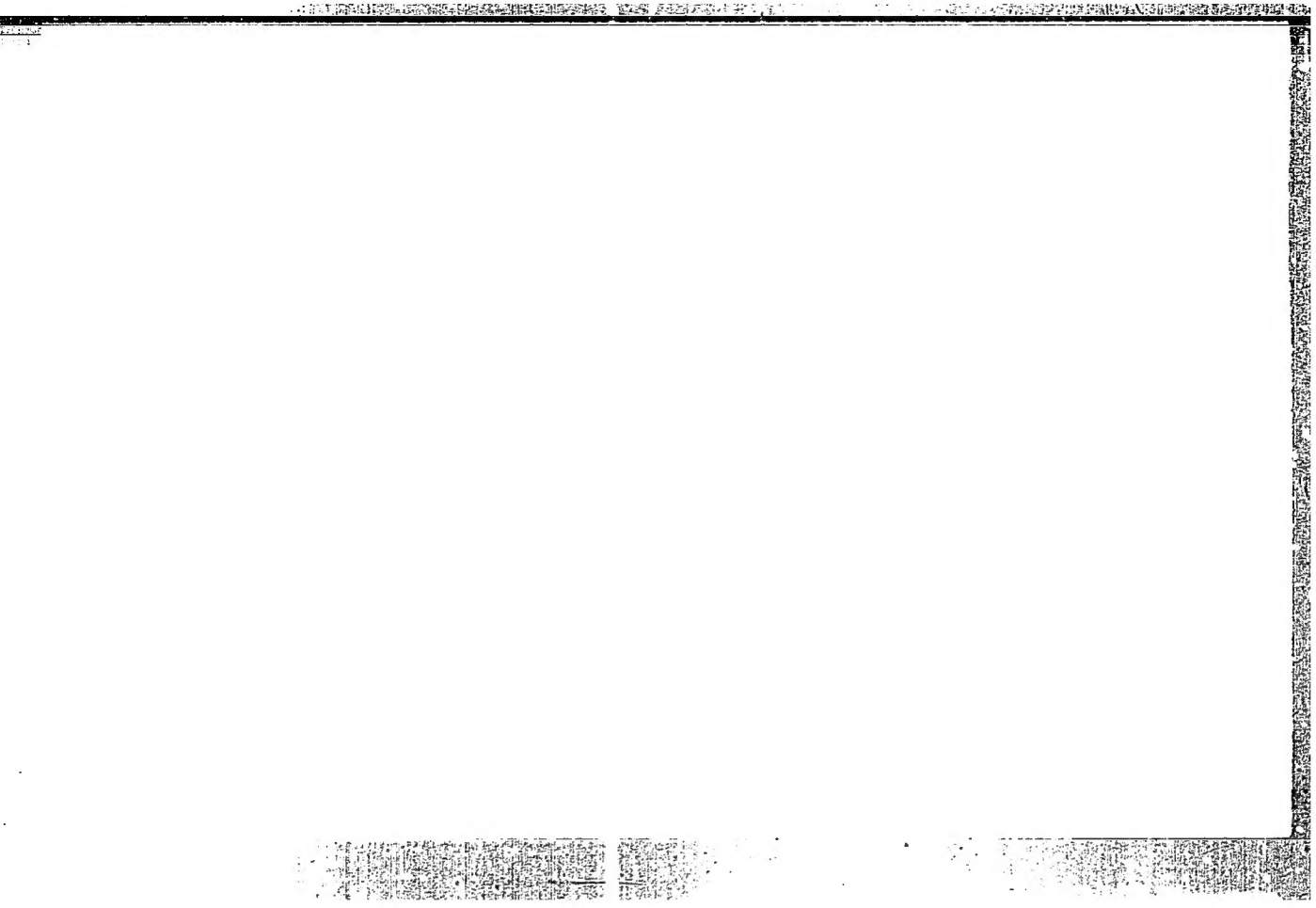
4/4

1. Institut fizich skoy khimii AN SSSR.



V 445. INVESTIGATION OF SECONDARY REACTIONS IN CRACKING OF HYDROCARBONS, USING C^{14}. Andreev, E.A., Andrianova, T.I., Krylov, O.V., and Sakharov, M.M. (Dokl. Akad. Nauk SSSR (Rep. Acad. Sci. U.S.S.R.), 21 June 1955, vol. 102, (6), 1119-1122). Iso-octane was cracked at 500°C over an alumina-silica catalyst. In successive experiments radioactive methane, propane and isobutylene were added to the feed and the radioactivity of the reaction products was measured. The results showed that methane plays only a slight part in secondary reactions, while propane and isobutylene react in many ways, which include the destructive alkylation of iso-octane and the hydrogenation of isobutylene. (L).

(3)



APPROVED FOR RELEASE: 06/14/2000 CIA-RDP86-00513R000826820020-3"

KRYLOV, O V

USSR/Physical Chemistry - Kinetics. Combustion. Explosives. Topochemistry. Catalysis, B-9

Abst Journal: Referat Zhur - Khimiya, No 19, 1956, 61093

Author: Krylov, O. V., Roginskiy, S. Z.

Institution: None

Title: Concerning the Possible Mechanism of Catalytic Oxidation of Hydrogen on Metals

Original Periodical: Izv. AN SSSR, Otd. khim. n., 1956, No 2, 145-149

Abstract: Presented is a summary of principal results of studies of kinetics of oxidation of H_2 on Pt. It is assumed that the stage which limits the process of oxidation of H_2 on Pt is the adsorption of O_2 without breach of molecules into atoms. Oxygen having undergone strong surface combination (probably in the form of ions) with the participation of d-electrons of Pt is not reduced by H_2 but activates Pt as concerns the reaction of oxidation of H_2. H_2 is adsorbed at these active centers of Pt, reversibly poisoning them. The

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USSR/Physical Chemistry - Kinetics. Combustion. Explosives. Topochemistry. Catalysis, B-9

Abst Journal: Referat Zhur - Khimiya, No 19, 1956, [illegible]093

Abstract: assumption is made concerning the possible role of ions and radicals during the subsequent stages of the process. Regularities of oxidation of H_2 on Pt are retained also in the case of Pd and other noble metals, which makes probable the existence of a single mechanism. Bibliography, 33 titles.

Card 2/2

[redacted], O.V.

USSR/Physical Chemistry - Thermodynamics. Thermochemistry. B-8
Equilibrium. Physico-Chemical Analysis. Phase Transitions

Abs Jour : Referat Zhur - Khimiya, No 2, 1957, 3734

Author : Kirillov I.P., Krylov O.V., Alekseyev A.M.
Inst : Ivanovo Chemico-Technological Institute
Title : Study of Physicochemical Properties of System PbO Fe_2O_3.

Orig Pub : Tr. Ivanovsk. khim.-tekhnol. in-ta, 1956, No 5, 61-68

Abstract : Stuly of PbO-Fe_2O_3 system produced by co-precipitation of the hydroxides from a mixture of nitrates of Fe and Pb, with NH_3. After a preliminary drying (90-120°) the system was calcined within 200-800 range at intervals of 100°. In the course thereof were investigated the magnetic susceptibility, adsorption power and solubility (relative rate of dissolution of Fe_2O_3 in 1.0 N HCl and PbO in 0.25 N CH_3COOH. It was found that the system under study passes through a series of intermediate states

Card 1/2 - 83 -

USSR/Physical Chemistry - Thermodynamics. Thermochemistry. B-8
Equilibrium. Physico-Chemical Analysis. Phase Transitions

Abs Jour : Referat Zhur - Khimiya, No 2, 1957, 3734

on calcining: 1) Decomposition of nitrates and hydroxides (100-350°); 2) Crystallization and polymorphous transformations of PbO and Fe_2O_3 (350-500°); 3) Internal diffusion, characterized by incorporation of more mobile molecules of PbO into the crystal lattice of Fe_2O_3 (500-700°); 4) Formation of crystalline reaction product -- lead ferrite $PbO.Fe_2O_3$ (700-800°).

Card 2/2 - 84 -

USSR/Physical Chemistry - Kinetics. Combustion. Explosives. Topochemistry.

Abstract

USSR/ Physical Chemisty - Kinetics. Combustion. Explosives. Topochemistry. Catalysis B-9

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11284

Author : Krylov O.V., Roginskiy S.Z., Fokina Ye. A.
Inst : Department of Chemical Sciences, Academy of Sciences USSR
Title : Study of the Dependence of Catalytic Activity of Binary Compounds of Metals of the Second Group with Non-Metals Upon the Position of Elements in the Periodic System of Mendeleyev. Communication 1. Catalytic Decomposition of Isopropyl Alcohol over Oxides of Alkaline-Earth Metals.

Orig Pub : Izv. AN SSSR, Otd. khim. n., 1956, No 6, 668-675

Abstract : In a flow-unit, at 314-460°, a study was made of decomposition of isopropyl alcohol in the presence of the catalysts CaO (I), SrO (II), BaO (III), $CaCO_3$ (IV), $BaCO_3$ (V) or $Ca(OH)_2$ (VI). In the I-III series catalytic activity of the oxides increases. Over all the oxides dehydrogenation of alcohol predominates over the dehydration. Energies of activation E of dehydrogenation (in cal/mole), I 12000-16000, on II 11000, on III 6000. Values of E of dehydration are higher (in cal/mole): on I 22000-26000, on II 25000, on III 12000. At the same time E values of dehydration

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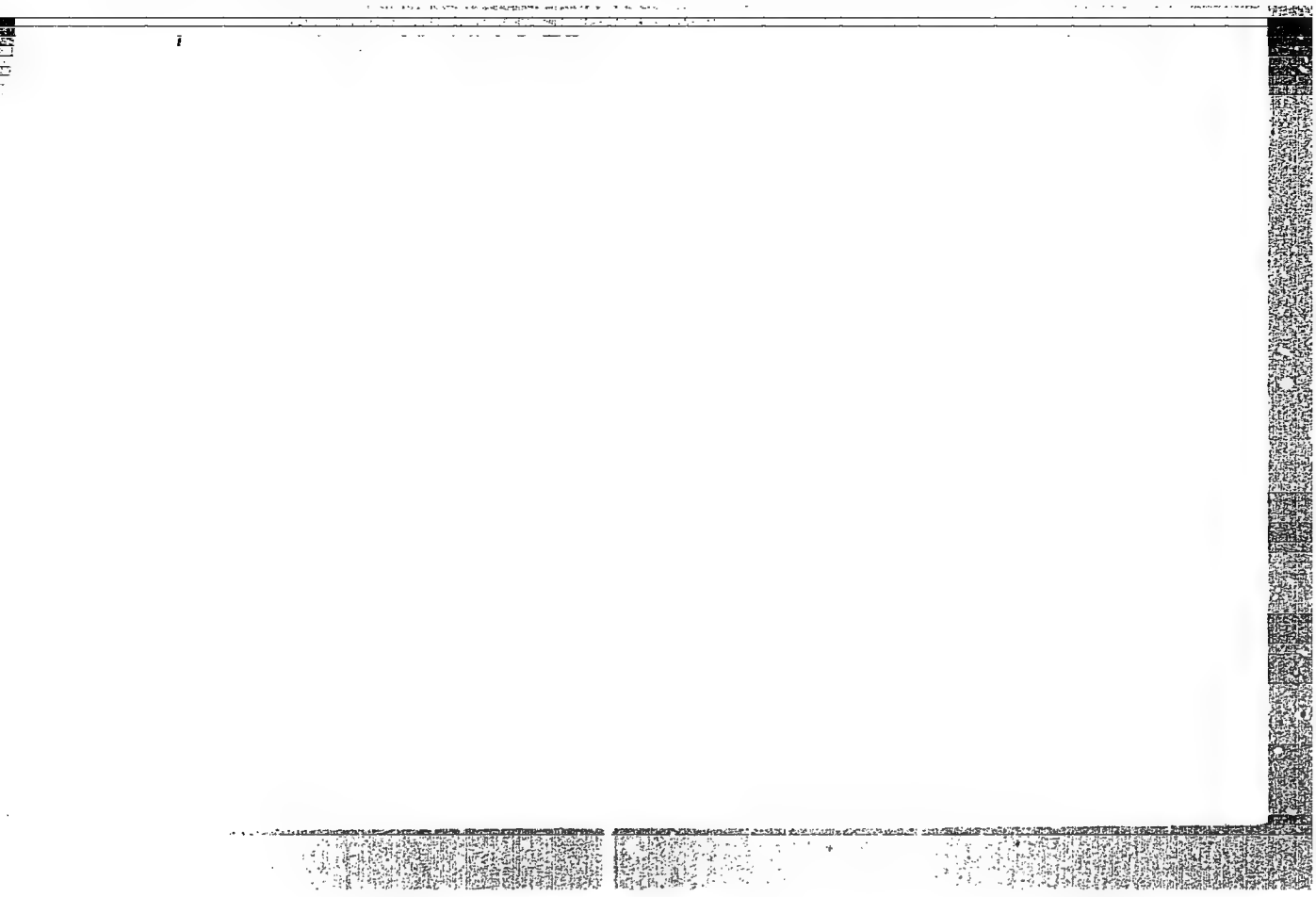
Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11284

over carbonates (24000 on IV, 17000 on V) are lower than dehydrogenation E values (39000 on IV, 26000 on V) and approximate the dehydrogenation E over oxides. On the basis of these data the assumption is made concerning the presence in oxides of carbonate admixtures which cause the dehydration. Dehydrogenation E over VI, of 16000 cal/mole, is close to dehydrogenation E over I. Literature data concerning catalytic properties of solid alkalies indicate widespread use of alkaline catalysis.



APPROVED FOR RELEASE: 06/14/2000 CIA-RDP86-00513R000826820020-3"

[redacted], M. V., [redacted], Yu. A.

"Study of the Acid-Base Properties of Catalytic Surfaces by the Differential Isotope Method."

KRYLOV, O.V.; ROGINSKIY, S.Z.; FOKINA, Ye.A.

Investigating the dependence of catalytic activity of binary metal compounds of the second group with nonmetals on the position of the elements in M.I.Mendeleev's periodic table. Report No.2: Catalytic decomposition of isopropyl alcohol on oxides of metals from the side subgroup of the second group. Izv.AN SSSR Otd.khim. nauk no.4:421-430 Ap '57. (MIRA 10:11)

1. Institut fizicheskoy khimii AN SSSR
(Catalysis) (Isopropyl alcohol) (Oxides)

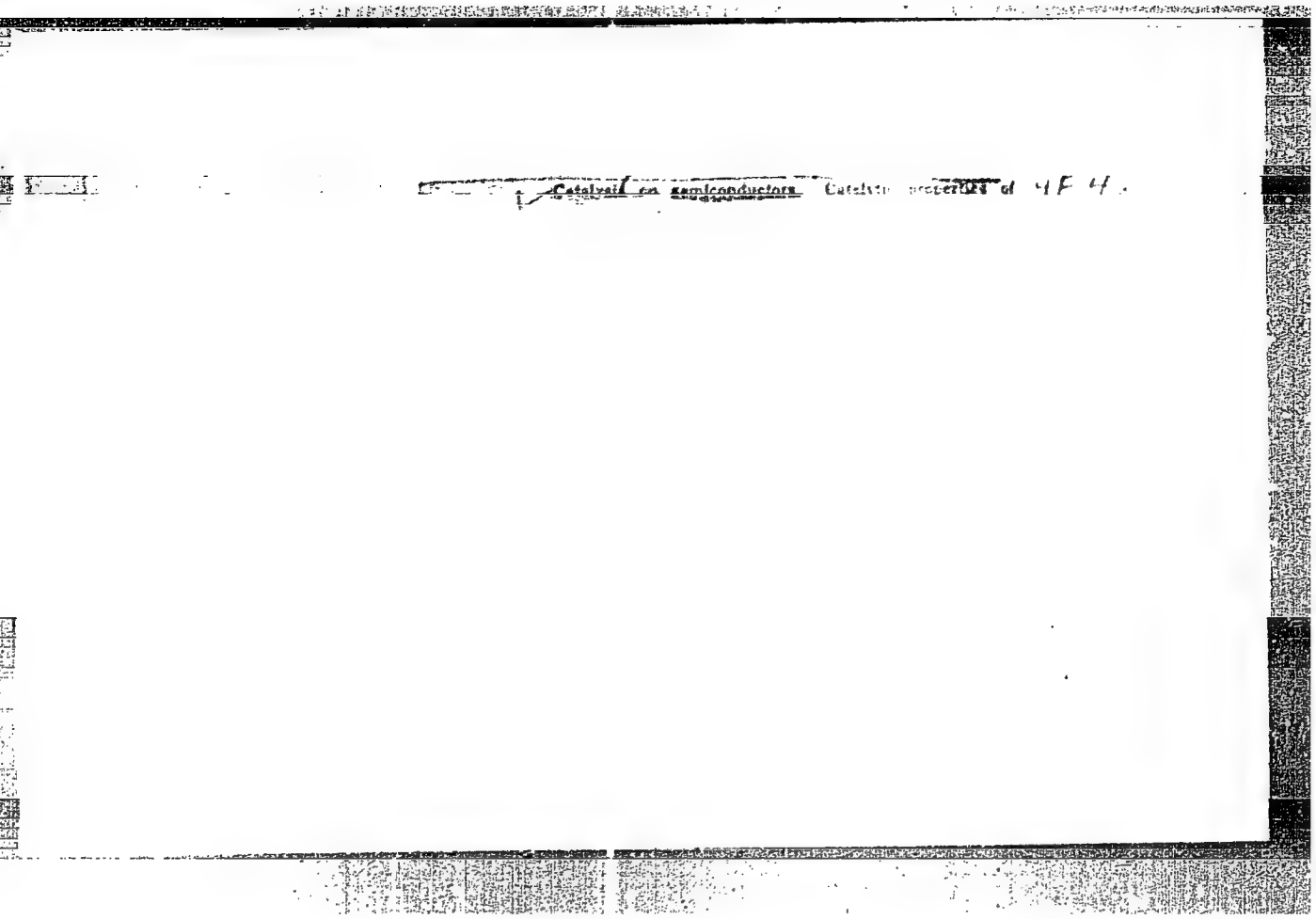
KRYLOV, O.V.; FOKINA, Ye.A.

Study of sulfide stability with the aid of S^{35} during catalytic decomposition of isopropyl alcohol. Probl. kin. i kat. 9:294-303 '57. (MIRA 11:3)

(Sulfides) (Catalysis) (Sulfur--Isotopes)

KRYLOV, O.V.; YOKINA, Ye.A.

Study of acid-base properties of catalytic surface by the differential isotope method. Probl. kin. i kat. 9:304-313 '57. (MIRA 11:3)
(Adsorption) (Cresol) (Carbon--Isotopes)



AUTHORS: Krylov, O. V., Fokina, Ye. A. 62-58-3-2/30

TITLE: The Investigation of the Catalytic Activity of the Binary Compounds of Metals of the Second Group With Nonmetals as Dependent on the Position of the Elements in the Mendeleyev Periodic System (Izucheniye zavisimosti kataliticheskoy aktivnosti binarnykh soyedineniy metallov vtoroy gruppy s nemetallami ot polozheniya elementov v periodicheskoy sisteme Mendeleyeva). Communication 3. The Catalytic Decomposition of Isopropyl Alcohol on the Sulfides of Metals of the Second Group (Soobshcheniye 3. Kataliticheskoye razlozheniye izopropilovogo spirta na sul'fidakh metallov vtoroy gruppy)

PERIODICAL: Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk, 1958, Nr 3, pp. 266-276 (USSR)

ABSTRACT: This paper represents part of the systematic investigations of the catalytic properties of binary metallic compounds (metals of the 2nd group) with metalloids of the 6th group. Beside the sulfides of the 2nd metal group some sulfide samples (of Pb and Bi) were also investigated. The present paper describes the investigation of sulfurous zinc ZnS and

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The Investigation of the Catalytic Activity of the Binary Compounds of Metals of the Second Group With Nonmetals as Dependent on the Position of the Elements in the Mendeleyev Periodic System. Communication 3. The Catalytic Decomposition of Isopropyl Alcohol on the Sulfides of Metals of the Second Group

62-58-3-2/30

similar types of zinc. Table 1 shows the results of the performed experiment. The dehydrogenation and dehydration of isopropyl alcohol on the sulfides were also investigated (see tables 3-6). It became evident that all investigated sulfides except PbS are dehydrogenizing catalysts. The catalytic activity of the sulfides Zn and Cd is higher than that of ZnO and CdO. It was further found that a modification of the method of synthesis of the sulfide causes a modification of its catalytic properties. Under the conditions of the decomposition of isopropyl alcohol (in the layer) the activity of ZnS is higher than of ZnO. The activation energy of the dehydrogenation (in the layer) increases with an increasing filling of the surface. There are 8 figures, 6 tables, and 17 references, 16 of which are Soviet.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR (Institute for Physical Chemistry, AS USSR)

SUBMITTED: January 8, 1957

Card 2/2

SOV/30-58-7-34/49

AUTHOR: Krylov, O. V., Candidate of Chemical Sciences

TITLE: Physics and Physical Chemistry of Catalysis (Fizika i fiziko-khimiya kataliza) Transactions of the All-Union Conference (Vsesoyuznaya konferentsiya)

PERIODICAL: Vestnik Akademii nauk SSSR, 1958, Nr 7, pp. 119 - 122 (USSR)

ABSTRACT: This conference convened in Moscow between March 20th and March 23rd. It was called by the Department of Chemical Sciences and the Institute of Physical Chemistry of the AS USSR (Otdeleniye khimicheskikh nauk i Institut fizicheskoy khimii Akademii nauk SSSR). It was attended by more than 600 persons from different towns of the Soviet Union as well as from countries of the people's democracies. Nearly 100 reports were submitted, 78 of which were given to the participants for discussion. The remainder was read. The following reports were heard:

1) S. Z. Roginskiy, (Institute of Physical Chemistry, AS USSR), spoke about the selective methods concerning semiconductor catalysis.

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2) V. V. Boldyrev, Tomsk University, used electron representations for the explanation of the course of topochemical reactions.
3) N. P. Keyyer, (Institute of Physical Chemistry, AS USSR), used electron representations for the clarification of the characteristics of heterogeneity of the active surface of semiconductor contacts.
4) F. F. Vol'kenshteyn, V. B. Sandomirskiy and Sh. M. Kogan, (Institute of Physical Chemistry, AS USSR), investigated the influence of exposure as well as of an external electric field on the absorptive power of a semiconductor.
5) A. N. Terenin spoke about the investigation of the structure and the behavior of surface formations in the case of adsorption and catalysis.
6) V. F. Kiselev (Moscow University), dealt with problems concerning the elementary act of catalysis.
7) G. K. Boreskov, Physical-Chemical Institute imeni L. Ya. Karpov (Fiziko-khimicheskiy institut im. L. Ya. Karpova), reported on the dependence of the catalytic activity of metals on their position in the periodic system of elements.

8) V. L. Bonch-Bruyevich and V. B. Glasko, (Moscow University), reported on the results of the adsorption computation of metals.

9) A. A. Balandin, Institute of Organic Chemistry AS USSR (Institut organicheskoy khimii Akademii nauk SSSR), reported on new data concerning the rôle played by structure factors in heterogeneous catalysis.

10) V. V. Voyevodskiy disproved his (and N. N. Semenov's) hypothesis of the existence of surface lattices and a heterogeneous catalysis.

11) Ya. T. Eydus and N. I. Yershov, (Institute of Organic Chemistry, AS USSR), O. A. Golovina, M. M. Sakharova, S. Z. Roginskiy and Ye. S. Dokukina, (Institute of Physical Chemistry, AS USSR), proved the existence of polymerization lattices in heterogeneous-catalytic processes of hydrocarbon synthesis.

12) N. N. Tikhomirov, P. N. Bubnov and V. V. Voyevodskiy, (Institute of Chemical Physics, AS USSR), reported on the application of the method of paramagnetic resonance of electrons for the purpose of investigating the interaction

of molecular oxygen with the free carbon valences.

13) Ya. K. Syrkin, (Institute of General and Inorganic Chemistry AS USSR) (Institut obshchey i neorganicheskoy khimii Akademii nauk SSSR), reported on problems concerning the molecular mechanism in catalysis.

14) K. V. Topchiyev, Moscow University, gave a survey on the data concerning catalytic activity of aluminum silicates.

15) L. I. Piguzova and M. A. Kaliko, All-Union Scientific Research Institute of Mineral Oil Industry (Vsesoyuznyy nauchno-issledovatel'skiy institut neftyanoy promyshlennosti) reported on problems concerning characteristics of active acid centers in cracking and in catalytic reactions with aluminum silicates.

16) N. M. Chirkov, Institute of Chemical Physics, AS USSR, proved the proton character of the mechanism of homogeneous acid catalysis.

17) O. V. Krylov, Institute of Chemical Physics, AS USSR, spoke about the heterogeneous catalysis of acids.

18) G. M. Zhabrova, V. I. Vladimirova and Ye. I. Yegorov, Institute of Physical Chemistry, AS USSR, spoke about the sorption of ions in the production of a zinc oxide catalyst.

Physics and Physical Chemistry of Catalysis. Transactions of the All-Union Conference

SOV/ 3o-58-7-34/49

19) O. M. Poltorak, Moscow University, reported on problems concerning the genesis of catalysts.

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5(4) SOV/62-58-12-3/22

AUTHORS: Krylov, O. V., Kushnerev, M. Ya., Fokina, Ye. A.

TITLE: Investigation of the Dependence of the Catalytic Activity of Binary Compounds of Metals of the Second Group With Non-Metals Upon the Position of the Elements in the Mendeleyev Periodic System (Izucheniye zavisimosti kataliticheskoy aktivnosti binarnykh soyedineniy metallov vtoroy gruppy s nemetallami ot polozheniya elementov v periodicheskoy sisteme Mendeleyeva) Communication 4: Catalytic Decomposition of Isopropyl Alcohol on Zinc Selenide and Telluride (Soobshcheniye 4. Kataliticheskoye razlozheniye izopropilovogo spirta na selenide i telluride tsinka)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1958, Nr 12, pp 1413-1421 (USSR)

ABSTRACT: The present paper deals with the investigation of the catalytic activity of selenides and tellurides of metals of the second group with respect to the dehydration and dehydrogenation of isopropyl alcohol. It is a continuation of the investigations carried out with the oxides and sulfides of metals of the same group (Refs 1-3). The investigation methods employed are de-

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Investigation of the Dependence of the Catalytic Activity of Binary Compounds of Metals of the Second Group With Non-Metals Upon the Position of the Elements in the Mendeleyev Periodic System. Communication 4: Catalytic Decomposition of Isopropyl Alcohol on Zinc Selenide and Telluride

scribed (Refs 1-3). The ZnSe preparation was supplied by M. S. Belen'kiy, the ZnTe preparation by N. A. Goryunova, and chemically pure tellurium by A. V. Novoselova. The decomposition of isopropyl alcohol on ZnSe and ZnTe within the temperature range 20-140° was investigated. It was found that the reaction in principle develops in the direction of dehydrogenation. In the reaction a decrease of the catalytic activity of ZnSe and ZnTe is observed. The activation energy of the dehydrogenation of alcohol on ZnSe increases from 15 to 21 kcal/mol. The ZnSe sample annealed in air at 600° was less active than that not annealed. Elementary tellurium has a low catalytic activity. Radiographic and electronographic investigations as a result of comparison of thermodynamic characteristics showed that the phase changes of the catalyst are due to impurities in the basic sample and on temperature effects, but in no case on the course of catalysis. There are 11 figures, 3 tables, and 10 references, 7 of which are Soviet.

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SOV/62-58-12-3/22

Investigation of the Dependence of the Catalytic Activity of Binary Compounds of Metals of the Second Group With Non-Metals Upon the Position of the Elements in the Mendeleyev Periodic System. Communication 4: Catalytic Decomposition of Isopropyl Alcohol on Zinc Selenide and Telluride

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR (Institute of Physical Chemistry, Academy of Sciences, USSR)

SUBMITTED: June 1, 1957

Card 3/3

Krylov, O.V.

AUTHORS: Krylov, O. V., Roginskiy, S. Z. Corresponding 20-3-30/59
Member AN USSR

TITLE: Catalysis on Intrinsic Semiconductors (O katalize na poluprovodnikakh v oblasti sobstvennoy provodimosti)

PERIODICAL: Doklady AN SSSR, 1958, Vol. 118, Nr 3, pp. 523-525 (USSR)

ABSTRACT: Although the same mechanism of the primary act of the interaction of a semiconductor-catalyst with the substrate prevails the catalysis in the domain of intrinsic conduction must differ in many regards from the catalysis in the domain of the admixture-conduction. For the catalysis in the domain of intrinsic conduction the following must be characteristical: 1) A light dependence of the catalytic activity on the "structure-sensitive" properties; 2) A connection between the catalytic properties and the substance properties; 3) A connection between the catalytic properties and the width of the forbidden zone, which results from this; 4) High values of the factor in front of the exponential function; 5) A compensation of the differences between the n- and the p--semiconductors. The data which were obtained by the authors

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together with Ye. A. Fokina are given in a table, they show the sharp increase of the catalytic activity with regard to the dehydration of the isopropyl-alcohol at the transition from ZnO to ZnTe. At the same time the activation energy of the dehydration decreased, whereby this activation energy depends much on the filling up. The rate of dehydration was low, in case of all catalysts, whereby the percentage of dehydration decreased at the transition from ZnO to ZnTe. When the other properties in the series ZnO → ZnS → ZnSe→ →ZnTe were investigated the following could be stated: The catalytic activity and the dielectric constant ε increase, but the difference of the electron negativity and the width of the forbidden zone decrease. An exception in this view is ZnO with U = 3,2 eV. The catalysis takes place in a temperature range, in which are at least 3 of the here examined binary compounds (ZnS, ZnSe, and ZnTe) in the domain of intrinsic conduction. At the same time with the increasing of the dehydrating activity the lattice parameter of the ZnS increases. Thus in the case of the here examined binary compounds a simpler correlation between the width of the forbidden zone and the catalytic activity is observed. Such investigations would be desirable also for other groups

Catalysis on Intrinsic Semiconductors 20-3-30/59

of compounds. There are 1 figure and 19 references, 15 of which are Slavic.

ASSOCIATION: Institute for Physical Chemistry AN USSR (Institut fizicheskoy khimii Akademii nauk SSSR)

SUBMITTED: September 9, 1957

AVAILABLE: Library of Congress

Card 3/3

SOV/20-120-2-30/63

AUTHORS: Krylov, O. V., Fokina, Ye. A.

TITLE: On the Catalytic Properties of Calcium Oxide (O kataliticheskikh svoystvakh okisi kal'tsiya)

PERIODICAL: Doklady Akademii nauk SSSR, Vol. 120, Nr 2, pp. 333 - 335 (USSR)

ABSTRACT: First, reference is made to various pertinent papers published previously. The investigation of the rules governing the basic catalysis as against the acid catalysis and the oxidation-reduction catalysis is very interesting. The dehydration of cyclohexane, the decomposition of isobutyl alcohol and of hydrazines on calcium oxide is investigated. The calcium oxide was produced by a dehydration of $Ca(OH)_2$ at 600° in a vacuum in the same container, in which the catalytic reaction was investigated. The reaction products were analyzed by freezing out. Besides, an additional analysis for H_2 was carried out. The hydrogen was made to pass through a palladium capillary. The kinetic curves of the dehydration of isopropyl alcohol in the adsorbed layer at 100-200° are given in a diagram. The amount

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of desorbed hydrogen at 180-200° is equal to the amount of acetone. At lower temperatures a 10-20% excess of hydrogen is found. This is explained by the more pronounced adsorption of acetone on CaO. With an initial pressure of C_6H_{12} amounting to 0,2 mm the dehydration of cyclohexane proceeds at 300-450° with a satisfactory velocity. Further details are given. These results are well reproducible. The activation energy of dehydration is 30,5 Kcal/ mol. A stoichometric decomposition of C_6H_{12} into $C_6H_6 + 3H_2$ was not observed. In another diagram the kinetic curves of the decomposition of hydrazine upon the absorbed layer at 50-200° are given. This investigation proves that it is possible to carry out three reactions of hydrogen separation upon CaO. Two of these reactions, the dehydration of alcohol and of cyclohexane proceed in the same direction as upon electron semiconductors. The direction of the third reaction, the decomposition of hydrazine differs from the direction taken by the reaction upon metals and semiconductors. The authors express their gratitude to the Corresponding Member AS USSR, S.Z.Roginskiy for his advice and a number of valuable suggestions. There are 4 figures and 13 references, 9 of which

On the Catalytic Properties of Calcium Oxide SOV/20-120-2-30/63

are Soviet.

PRESENTED: January 2, 1958, by S.I.Vol'fkovich, Member, Academy of Sciences, USSR

SUBMITTED: December 31, 1957

1. Calcium oxide--Catalytic properties

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SOV/62-59-1-3/38

5(4)
AUTHORS: Krylov, O. V., Roginskiy, S. Z.

TITLE: The Dependence of Catalytic Activity of Binary Compounds of Metals of the Second Group With Non-Metals on the Position of Elements in Mendeleyev's Periodic System (Izucheniye zavisimosti kataliticheskoy aktivnosti binarnykh soyedineniy metallov vtoroy gruppy s nemetallami ot polozheniya elementov v periodicheskoy sisteme Mendeleyeva)Communication V. Regularities in the Change of Properties of the Series ZnO, ZnS, ZnSe, ZnTe (Soobshcheniye 5. O zakonomernostyakh izmeneniya svoystv v ryadu ZnO, ZnS,ZnSe,ZnTe)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 1, pp 17 - 24 (USSR)

ABSTRACT: The connection between the position of elements within the solid body in the periodic system on the one hand and the catalytic properties of this body on the other hand is insufficiently investigated. Systematic papers hitherto published primarily refer to simple bodies and mainly deal with explaining the role played by empty points of d-shells of the atom in catalysis. In view of the development of

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semiconductor chemistry and the connection between their electronic and catalytic properties, which frequently has been observed, it seemed to be important to investigate the effect exercised by the non-metallic component upon the latter. Nor have there been any experimental data available which might serve as basis for generalizations. In some earlier papers the authors tried to fill this gap by investigating the catalytic properties of semiconductors. The results obtained and data recently published indicate certain regularities which in future might be of general importance. In the present paper the authors investigated the effect of non-metal referring to the compound of the type $A^{II}B^{VI}$ with zinc as a positively charged atom A^{II}. In order to determine the corresponding regularities they compared the change in the catalytic properties in the series ZnO → ZnS → ZnSe → ZnTe as to the decomposition of isopropyl alcohol with the changes of a number of electric

characteristics of these semiconductors. It was stated that the catalytic activity of the binary MeX compound changes as to the dehydrogenation of alcohol simultaneously with the change of binding polarity which becomes manifest by the change of a number of electric properties. On the increase of the atomic weight of the non-metal in the MeX compound the activation energy of the dehydrogenation of alcohol decreases, whereas dielectric constant increases, and the width of the danger zone as well as the difference of electronegativity decreases. The dependence is complicated by the change of E (activation energy) with the occupation of the surface. According to data of publications it was assumed that the catalysts ZnS, ZnSe, ZnTe (possibly also ZnO) primarily act within the range of their own conductivity. Definite conclusions can be drawn only when electric properties of semiconductors during catalysis have been measured. It is supposed that the position of the level of impurity conductivity may be also determined according to the

position of elements (of which the semiconductor is made up) in the periodic system. The authors thank F. F. Vol'kenshteyn and V. B. Sandomirskiy for the discussion. There are 1 table and 31 references, 20 of which are Soviet.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR (Institute of Physical Chemistry of the Academy of Sciences, USSR)

SUBMITTED: May 31, 1957

5.3200

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66869

AUTHORS: Krylov, O.V., Fokina, Ye.A. SOV/76-33-11-31/47

TITLE: Investigation of Some Catalytic Reactions on the Surface of Calcium Oxide

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 11, pp 2555-2558 (USSR)

ABSTRACT: In continuation of a previous paper (Ref 1) the authors investigated the decomposition of isopropanol and hydrazine as well as the dehydration of ethane and cyclohexane on calcium oxide. The decomposition of isopropanol was carried out in an adsorbed layer according to a method described earlier (Ref 2). The curves (Fig 1) are given of the decomposition of isopropanol at freezing out (-116°C) of the reaction products (acetone), in which case in the gas remained mainly hydrogen and the product of dehydrogenation, propylene. The hydrogen content was at 100°C - 64.3%, at 150°C - 74.6%, at 180°C - 78.8% and at 200°C - 84.0 -86.3%. The activation energy varied at 100-150°C in dependence on the degree of filling in the range, 21-30 kcal/mol and at 180-200°C from 32 to 36 kcal/mol. Ethane did not show any change on calcium at 0.4 mm Hg up to 600°C, above 600°C a small degree of pressure

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Investigation of Some Catalytic Reactions on the Surface of Calcium Oxide

increase could be observed and hydrogen was found in the reaction products. The dehydrogenation experiments carried out with a cyclohexane put at disposal by G.V.Isagulyants, showed (Fig 3 kinetic decomposition curve at 400°C and varied initial pressure) that the dependence of the initial reaction rate is linear with the pressure of the cyclohexane (Fig 4). The activation energy of the dehydrogenation is 30.5 kcal/mol at 300-450°C which is in accordance with data by A.A.Balandin and I.I.Brusov (Ref 4), and M.Ya.Kagan and R.M.Flid (Ref 5). Hydrogen was determined as the dehydrogenation product. The hydrazine decomposition was also investigated in the adsorbed layer of the calcium oxide and it was established that at 50-200°C the main reaction products are hydrogen and nitrogen. There are 6 figures and 7 references, 6 of which are Soviet.

ASSOCIATION: Akademiya nauk SSSR, Institut fizicheskoy khimii, Moskva (Academy of Sciences, USSR, Institute of Physical Chemistry, Moscow)

Card 2/2

5 (3)

AUTHORS: Frolov, V. M., Krylov, O. V., Roginskiy, S. Z., Corresponding Member, AS USSR

SOV/20-126-1-29/62

TITLE: Catalytic Dehydrogenation of Ethanol on Germanium (Kataliticheskoye degidrirovaniye etanola na germanii)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 126, Nr 1, pp 107 - 110 (USSR)

ABSTRACT: Germanium is able to catalyze several redox reactions (Refs 1,2). The authors wanted to investigate the kinetics of some of these reactions in the case of various Ge-samples with different conductivity in the case of a concentration change of the current carriers within a wide range. This can facilitate the understanding of the mechanism of the semiconductor catalysis. The kinetics of the reaction mentioned in the title was investigated under static vacuum conditions in a quartz reactor. Powder with a specific surface of 0.05 - 0.1 m^2/g obtained by pulverization in the mortar in air served for this purpose. The Ge-powder was trained before the experiment at 650° or at 650°

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Catalytic Dehydrogenation of [redacted] Germanium SOV/20-126-1-29/62

and at 10^{-5} - 10^{-6} torr. The mentioned dehydrogenation was investigated at 200-270°. A reduction of the reaction rate (Figs 1:1-4 cursive) took place in the case of subsequently carried out ethanol compositions on Ge, trained at 850°. This was stopped after the fourth experiment. Beside hydrogen and acetaldehyde also ethylene was found to exist in the gas phase. Its content was reduced from experiment to experiment. The hydrogen pressure was in all experiments equal to the summed pressure of acetaldehyde and ethylene (accuracy 2-3%). The authors assume that the fresh Ge-surface adsorbs an oxygen molecule from ethanol (reaction I) thanks to its great affinity to oxygen. The covering of the Ge-surface with adsorbed oxygen leads to the breaking-off of the reaction (I). As late as from the fourth experiment on only the process of the catalytic dehydrogenation takes place on the Ge-powder. The chemosorption of oxygen was carried out after the fourth experiment in order to clarify the effect of a complete covering of the Ge-surface with oxygen. The curves 5-8 (Fig 1) belong to the subsequently carried out experiments. They describe the kinetics of the hydrogen separation under the given conditions. Since the pressure of the

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acetaldehyde formed on the oxidized surface surpasses considerably the hydrogen pressure the removal of the adsorbed oxygen according to the reaction (III) is to be assumed. The catalytic reaction (II) proceeds then on the surface free from oxygen. Thus, adsorbed oxygen can in the case of the system germanium--ethanol approach to the stationary activity of the catalytic dehydrogenation from the side of the surface free from oxygen as well as from the side of the surface completely covered by the adsorbed oxygen. Figure 1 shows the electronic characteristics of the alloyed Ge-samples, the logarithm of the pre-exponential multiplier (k_0) and of the seeming activation energy (E) of the catalytic ethanol dehydrogenation. The results described clarify to a certain extent the often discussed problem of the catalytic equivalence of the p- and n-semiconductors. The authors assume with a certain security with respect to the reaction mentioned in the title that the activation energies on the p-germanium are considerably lower than on n-germanium. This conclusion does, however, not hold in the case of all other reactions (Refs 6,7). The range of the investigated systems is to be widened and the catalytic processes are to be more tho-

roughly investigated. Data concerning the change of the electronic characteristics of the surface during the reaction process are to be used. There are 3 figures, 1 table, and 7 references, 4 of which are Soviet.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR (Institute of Physical Chemistry of the Academy of Sciences,USSR)

SUBMITTED: January 28, 1959

PHASE I BOOK EXPLOITATION SOV/3921

Akademiya nauk SSSR. Institut fizicheskoy khimii

Problemy kinetiki i kataliza. [t] 10: Fizika i fiziko-khimiya kataliza (Problems of Kinetics and Catalysis. [vol.] 10: Physics and Physico-Chemistry of Catalysis) Moscow, Izd-vo AN SSSR, 1960. 461 p. Errata slip inserted. 2,600 copies printed.

Eds.: S.Z. Roginskiy, Corresponding Member of the Academy of Sciences USSR, and O.V. Krylov, Candidate of Chemistry; Ed. of Publishing House: A.L. Bankvitser; Tech. Ed.: G.A. Astaf'yeva.

PURPOSE: This collection of articles is addressed to physicists and chemists and to the community of scientists in general interested in recent research on the physics and physical chemistry of catalysis.

COVERAGE: The articles in this collection were read at the conference on the Physics and Physical Chemistry of Catalysis organized by the Otdel khimicheskikh nauk AN SSSR (Section of Chemical Sciences, Academy of Sciences USSR) and by the Academic Council on the problem of "the scientific bases for the selection of catalysts." The Conference was held at the Institut fizicheskoy khimii AN SSSR (Institute of Physical Chemistry of the AS USSR) in Moscow, March 20-25, 1958. Of the great volume of material presented at the conference, only papers not published elsewhere were included in this collection.

III. SOME GENERAL PROBLEMS OF CATALYSIS

IV. ACID - BASE CATALYSIS

Krylov, O.V.

FROLOV, V.M.; KRYLOV, O.V.; ROGINSKIY, S.Z.

Catalytic properties of germanium. Probl. kin. i kat. 10:102-107 '60. (MIRA 14:5)

1. Institut fizicheskoy khimii AN SSSR.
(Germanium)

KRYLOV, O.V.; ROGINSKIY, S.Z.; FOKINA, Ye.A.

Catalysis on semiconductors in the region of natural conduction.
Probl. kin. i kat. 10:117-120 '60. (MIRA 14:5)

1. Institut fizicheskoy khimii AN SSSR.
(Catalysis) (Semiconductors)

KRYLOV, O.V.

Catalytic action of solid bases. Probl. kin. i kat. 10:273-278 '60.
(MIRA 14:5)

1. Institut fizicheskoy khimii AN SSSR.
(Catalysts) (Bases (Chemistry))

KRYLOV, O.V.; FOKINA, Ye.A.

Isotopic study of the heterogeneous surfaces of oxide catalysts used in the decomposition of isopropyl alcohol. Part 1: Calcium oxide. Kin. i kat. 1 no. 3:421-430 S-O '60. (MIRA 13:11)

1. Institut fizicheskoy khimii AN SSSR.
(Isopropyl alcohol) (Catalysts) (Carbon--Isotopes)

S/195/60/001/004/006/015
B017/B055

AUTHORS: Krylov, O. V., Fokina, Yo. A.

TITLE: Application of the Isotopic Exchange Method for the Investigation of Surface Inhomogeneity of Oxide Catalysts by Decomposition of Isopropyl Alcohol. II. Aluminum Oxide and Zinc Oxide

PERIODICAL: Kinetika i kataliz, 1960, Vol. 1, No. 4, pp. 542-547

TEXT: Studies on the nature of active centers on the surface of Al_2O_3 were carried out by N. P. Keyyer (Ref. 2), A. A. Babushkin and A. V. Uvarov (Ref. 3), and V. E. Vassorberg and A. A. Balandin (Ref. 4). By examining the decomposition of isopropyl alcohol on the layer adsorbed on aluminum oxide by the differential isotope method, they found that the aluminum-oxide surface was inhomogeneous. Dehydration of isopropyl alcohol occurs on only 4-6% of the aluminum-oxide surface. The results obtained by studying the dehydration of isopropyl alcohol on aluminum oxide appear in Figs. 1 and 2. The specific activity of all reaction

products desorbed during isopropyl-alcohol dehydration was found to be constant. Desorption and dehydration of isopropyl alcohol on Al_2O_3 is illustrated in Fig. 4. The kinetics of isotopic exchange between isopropyl alcohol adsorbed on Al_2O_3 and isopropyl alcohol in the gaseous phase is graphically shown in Fig. 3. The decomposition of isopropyl alcohol on zinc oxide was investigated by the differential isotope exchange method whereby both dehydrogenation and dehydration products of isopropyl alcohol were found to have constant but different specific activity levels. Fig. 5 gives a graphic representation of the results obtained at decomposition of isopropyl alcohol on ZnO. Dehydrogenation and dehydration of isopropyl alcohol occur at different active centers of the zinc oxide surface. Dehydration occurs mainly at active centers having a lower activation energy. The kinetics of isotopic exchange between isopropyl alcohol adsorbed on ZnO and isopropyl alcohol in the gaseous phase is shown in Fig. 6. Isotopic exchange reactions of isopropyl alcohol adsorbed on ZnO and Al_2O_3 are much delayed, thus indicating the

Application of the Isotopic Exchange Method for the Investigation of Surface Inhomogeneity of Oxide Catalysts by Decomposition of Isopropyl Alcohol. II. Aluminum Oxide and Zinc Oxide

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B017/B055

inhomogeneity of the active surface of the catalyst. There are 7 figures and 6 Soviet references.

ASSOCIATION: Institut fizicheskoy khimii AN SSSR (Institute of Physical Chemistry of the AS USSR)

SUBMITTED: March 23, 1960

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9,4300 (1143, 1150, 1160)
5.1190 2209, 1274, 1153

S/063/60/005/005/006/021
A051/A029

AUTHORS: Krylov, O.V., Candidate of Chemical Sciences, Frolov, V.M.

TITLE: Chemical Reactions on the Surface of Germanium, Silicon and Their Electronic Analogues

PERIODICAL: Zhurnal Vsesoyuznogo Khimicheskogo Obshchestva im. D.I. Mendeleyeva, 1960, No. 5, Vol. 5, pp. 535-543

TEXT: Although the chemical reactions, which take place on the surface of semiconductors, are of great practical significance, these surface properties have not been investigated, as well as those of the bulk. The following processes are included in chemical reactions taking place on the surface of a solid body: 1) chemical adsorption (chemosorption), 2) catalysis, 3) formations of new phases. The present article is dedicated to the analysis of chemosorption, formation of new phases connected with the aspects of chemosorption, and to a lesser degree to the catalytic reactions. A discussion is given on the electronic processes in chemosorption on semiconductors.

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Chemical Reactions on the Surface of Germanium, Silicon and Their Electronic Analogues

It is said that Soviet works (Ref. 6-9) have been published on this subject. The main aspects in this connection are listed: 1) A free electron (or free electron "hole") of the semiconductor lattice is the center of chemosorption. 2) Adsorption atoms and molecules are regarded as admixtures, destroying the strictly periodic structure of the lattice. 3) The adsorption ability and the catalytic activity of the semiconductor surface is determined by the mutual distribution of the local level of the adsorption particle and by the Fermi level (level of chemical potential) on the surface. 4) The position of the Fermi level on the semiconductor surface ε depends on the position of the Fermi level in the volume ε_0, and on the bend of the zones at the surface, i.e., the difference of potentials between the surface and volume $\Delta\varepsilon$ viz., $\varepsilon = \varepsilon_0 + \Delta\varepsilon$. 5) The position of the volume Fermi level (ε_0) at low temperatures is determined by admixtures introduced into the semiconductor. 6) The bend of the zones on the semiconductor surface ($\Delta\varepsilon$) is determined by its charging during adsorption and also by the non-adsorp-

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tion surface states (Tamm levels, surface defects). Several conclusions are drawn from these aspects, which were confirmed experimentally: The dependence of the adsorption and catalytic ability on the electroconductivity σ and the work of the electron escape φ of the semiconductor, and the reverse phenomenon: a change in σ and φ in the adsorption process and that of catalysis; the effect of admixtures introduced into the lattice of the semiconductor, i.e., so-called "modification" on the adsorption and catalysis, the opposite effect of the donor and acceptor admixtures, the appearance of kinetic anomalies in the adsorption and catalysis, etc. The authors refer to the question of the connection between the surface properties of semiconductors and the electronic structure of the atoms which constitute the surface, stating that this aspect has been only slightly investigated. Comments are made of Dowden's theory (Ref. 14) on this subject and that of Goryunova (Ref. 13). It is stated that most authors, with regard to the processes of chemosorption and catalysis, classify semiconductors according to their ability to capture some admixtures (semiconductors of the n- and p-

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type). Others consider the anomalous behavior with regard to the adsorption and catalysis of semiconductors with transition metals in their composition. It is pointed out that if the limiting stage of the surface chemical reaction is the interaction of the adsorption molecule and the free electron of the semiconductor, semiconductors of the n-type will speed up this reaction primarily, and then all the factors, which increase the concentration of the free electrons in the semiconductor, will increase the rate of reaction (Ref. 15). The conclusion is drawn from data derived in Ref. 15 that electrons of the lattice participate in the limiting stage of the reaction. Hauffe (Ref. 16) thinks that this stage may be the desorption of hydrogen:

$$\left.\begin{aligned} H_2(gas) &\rightleftharpoons 2H^+_{ads.} + 2e \\ D_2(gas) &\rightleftharpoons 2D^+_{ads.} + 2e \end{aligned}\right\} \quad \text{fast}$$

$$H^+_{ads.} + D^+_{ads.} + 2e \longrightarrow HD(gas) \qquad \text{slow.}$$

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The interest expressed by workers in recent years in the processes taking place on the surface of elementary semiconductors not containing d-electrons is pointed out (Ref. 17). It is further stressed that more research has been carried out on the subject of germanium, since it is widely used in semiconductor electrical appliances. A brief historical review of the development of scientific interest in chemosorption on germanium is given mentioning the early works of 1930 (Ref. 18) on the reaction of germanium nitride formation, also Ref. 19 on the decomposition of german (GeH_4) with the formation of dispersed germanium. Chemists showed interest in clarifying the interconnection between the chemical surface properties of the semiconductor with its electronic, volume and surface properties. Since Ge is covered with an oxide film in air, it is pointed out that prior to a chemosorption investigation a thorough purification of the Ge surface must be initially undertaken. Surface cleaning is based on combining the ionic bombardment with subsequent heating in a vacuum of 10^{-10} mm Hg. Other methods are: crushing single crystals in a vacuum (Ref. 21), reduction with hydrogen (Ref. 22,21), produc-

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tion of Ge films by evaporation in a vacuum (Ref. 23), cathode atomizing (Ref. 24) and decomposition (Ref. 25) of GeH_4. The compact single crystal samples are considered to be the most appropriate for measuring electrical properties, but difficulties arise due to the small surfaces. Ref. 26 is one of the first works on the investigation of the changes of the electrical properties as a result of contact of the sample with some gas at various pressures over a certain period of time. It was established that the contact potential of the surface can change reversibly between two extreme values differing by about 0.5 v with a change in the gas medium. Experimental results proved the existence of a layer of a space charge on the semiconductor surface determined by the surfaces states. The experimental results showed that even the most thorough purification of the surface by available methods does not lead to the disappearance of surface states. According to Handler (Ref. 27) the existence of surface states is determined by unsaturated bonds of the surface atoms of Ge. Fig. 2 shows the surface distribution of the Ge

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atoms for a crystallographic plane (III). The surface Ge atom becomes in the electrical respect similar to the atom with 5 electrons in the outer shell. The surface Ge atoms fulfill the role of acceptor levels. Any discrepancies in the results of the evaluation of the density of the surface states for the processed Ge surface by different methods is explained by the different densities of the unsaturated chemical bonds of the surface. An investigation of the electrical properties of the Ge surface, processed with a CP-4, (SR-4) scouring agent, showed the presence of a more complex structure of the surface states as compared to pure surfaces (Ref. 30). Several works were published on the acceptor nature of the first layer of adsorbed oxygen (Ref. 27,32,33). Ref. 33 showed that the contact of a pure Ge surface with oxygen at a pressure of 10^{-6} mm Hg causes an increase in the work performed by the escaping electron by 0.2 ev, whereby the equilibrium value of the work is reached within a few minutes. A study of the adsorption on single crystalline samples proved the electron-graphical methods using slow

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electrons to be very promising (Ref. 20). The authors of this work obtained a relationship for the connection of the intensity of the beam with a coating: $I/I_0 = (1 - \theta)^2$ (2), where I and I_0 are the intensities of the beam for the partially covered and pure surfaces, respectively, θ is the specific filling. If the kinetics of the adsorption is described by the expression: $\theta = 1 - e^{-\alpha Spt}$ (3), where α is the number of impacts of the gas molecules on the surface per second at 1 mm Hg relative to one surface atom of Ge, S the probability of adsorption in the impact of the gas molecule against the pure surface, p the pressure and t the time. Combining this expression with the previous one, the authors could trace the kinetic adsorption according to the change in the intensity of the electronic beam with time. These data correspond to the postulation of the constant activation energy and to the rate of adsorption being proportional to the products of the adhesion coefficient and part of the uncovered surface. Further reference is made to the work of Green (Ref. 28), where equation 3 is used for the description of the chemosorption kinetics of oxygen on germanium. A mano-

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metric study was made of the chemosorption kinetics of oxygen on Ge powder obtained by crushing in a high vacuum (Ref. 21). Green's publication (Ref. 28) assumes that the slow adsorption of oxygen described by the Roginskiy-Zel'dovich equation: $dN/dt = ae^{-bN}$ (6), where N is the amount of oxygen adsorbed at the time moment t, a and b are constants for the given temperature and pressure, begins with the filling. It is stated that on the basis of the kinetics of the slow adsorption of oxygen by Ge, it is difficult to form a conclusion of the exact mechanism of this process, since various types of mechanisms of interaction between a solid body and a gas may lead to the law of logarithms. In studying the kinetics of the chemosorption of oxygen on single crystal plates of Ge by the weight method data were obtained which coincided with Green's results (Ref. 35). It was found that the drop in the adsorption heat of the oxygen with filling according to Green was determined by repulsion forces between the adsorbed atoms. Other investigations undertaken are listed as follows: The adsorption of N_2, H_2, CO and CO_2, at —196, —78 and 25°C on single crystal Ge rods by the spark method; the high tem-

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perature oxydation of Ge, the chemosorption of hydrogen on Ge at high temperatures; the chemosorption of ammonia at 278°C on a Ge film; the adsorption of H_2, CO and O_2 on Ge powders; the adsorption of a number of gases in the crushing of single crystal Ge of the n-type results of the latter are given in Table 1 (Refs. 38,39,40,41,42,43,22,44). In all cases where adsorption was observed, it took place quickly before filling close to the monolayer. The cause of gas adsorption (except of pyridine and dioxane) is assumed to be the electrostatic interaction between the dipoles of the molecules of the adsorbate and the Ge surface. The authors exclude the possibility of valency bond formation in the adsorption of the investigated gases on Ge, since the latter calls for the dissociation of the gas molecules which invariably leads to $\theta < 1$. An analysis is given of the chemosorption on silicon and other electronic analogues of Ge. An investigation was made of the O_2 chemosorption on thread-like single crystal samples of silicon by the spark method (Ref. 46,48). Recently in semiconductor electronics semiconductors

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have been applied in addition to Ge and Si, which also did not contain d-electrons and were formed by elements equidistant from the fourth group: $A^{III}B^{V}$, $A^{II}B^{VI}$. The processes of gas etching of this type of semiconductor were investigated (Ref. 52). Syngrov (Ref. 54) studied the electrical properties of the surface of the $A^{III}B^{V}$ compounds. By measuring the effect of the field in samples of single crystals AlSb, InSb and GaSb of the n-type, it was shown that inversion layers are formed on the surface of these semiconductors connected with the presence of surface acceptors (Fig. 1). Certain facts, such as the high value of the field effect on the AlSb in a vacuum as compared to air, indicate a high influence of the adsorption on the electrical properties of semiconductors of this type. No definite answer has as yet been obtained on the difference in the chemosorption properties of n- and p-semiconductors. It was shown (Ref. 55,56) that additions of Li_2O and Ga_2O_3 to ZnO hardly affect the rate and energy of activation of the H_2 chemosorption. Similar results were obtained for the catalytic activity of the latter in the dehydration of C_4H_8. Reference is also made to the works of

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Chizhikova (Ref. 57), Kutseva (Ref. 58), on the study of the chemosorption of CO and O_2 on ZnO and NiO. Several examples are listed when the limiting stage of the chemosorption in catalysis is not the electronic interaction of the adsorbed molecule with the semiconductor. Some authors assume that the limiting stage is the movement of the active centers - structural defects - from the volume to the ZnO surface. Finally, the author discusses the catalytic reactions of the Ge surface and that of its analogues. The catalytic properties of Ge are mentioned quoting Refs. 25, 59. Conclusions were formed that the rate of reaction of the auto-catalytic decomposition of GeH_4 on a Ge film is controlled either by the dissociation of adsorbed radicals of GeH_x ($x = 2$ or 3) or by the desorption of oxygen when the surface is completely covered by the GeH_x radicals and hydrogen. The kinetics of the reaction $H_2 - D_2$ exchange on Ge powders obtained by crushing of single crystals in air with subsequent reduction by hydrogen were studied (Ref. 60,61). The ortho-para conversion of hydrogen and $H_2 - D_2$ exchange on Ge films produced by the cathode atomization in an interval of 77 - 175°C was investi-

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gated (Ref. 24). A comparison of the rates of these two reactions led the authors to the conclusion that the first one is of a magnetic or chemical nature. The authors of this article and Roginskiy investigated the catalytic properties of Ge on an example of dehydration of alcohols, cyclohexane, decomposition of hydrazine reactions on powders and films. The results showed that Ge is an active catalyst in the respective reactions. A study was also made of the kinetics of the catalytic reactions on n- and p- Ge with various admixture contents (Sb or Ga). Fig. 3 shows the relationship of the apparent activation energy of dehydration of C_2H_5OH to the concentration of the main charge carriers. From Refs. 65, 66 regarding the hydration reaction of ethylene and formic acid decomposition, it was also found that the hole samples were more active in the catalytic sense and were characterized by a lower activation energy than the electronic ones. A study was made of the decomposition of HCOOH on AlSb and InSb. The hole sample had a lower activation energy than the electronic ones. Fig. 4 shows the relationship of the catalytic activity at 200°C relative to a unit of surface for the decom-

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position of C_3H_7OH to the width of the forbidden zone. Data obtained from chemical reactions on the surface of Ge and its electronic analogues point to the faulty deductions presented in Refs. 14, 16, maintaining the all-important role of transition elements in chemosorption and catalysis. There are 3 tables, 2 diagrams, 2 figures and 73 references; 24 are Soviet, 42 are English, 7 are German.

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5(4)

68617

AUTHOR: Krylov, O.V.

S/020/60/130/05/030/061
B004/B014

TITLE: A Case of Homogeneous Continuation of a Heterogeneous Catalytic Reaction

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol 130, Nr 5, pp 1063-1066 (USSR)

ABSTRACT: In reference 1 the author had studied the decomposition of hydrazine on metallic, semiconductor, saltlike, acid, and basic catalysts. $N_2H_4 + L \longrightarrow NH_2\text{-}L + (\dot{N}H_2)_{adsorb}$ (L= free radical on the catalyst surface, NH_2-L = solid, bielectronic bond on the catalyst surface) was assumed to be the primary reaction on the catalyst surface on the basis of thermochemical calculations carried out in analogy to the calculation of N.N. Semenov (Ref 2) and V.V. Voyevodskiy (Ref 3). Next, chain and radical reactions follow on the catalyst surface the scheme of which is given. In order to give a direct proof of the chain reaction, the author studied the problem as to whether the reaction passes from the catalyst surface into the volume of the reaction vessel at temperatures at which the radicals $\dot{N}H_2$, $\dot{N}_2H_3$, and H· are no

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longer bound to the surface by adsorptive forces. The investigation was carried out by separate calorimetration according to M.L. Bogoyavlenskaya and A.A. Koval'skiy (Ref 5) in a molybdenum-glass apparatus designed by P.Yu. Butyagin and L.Ya. Margolis (Ref 6). Iron, ammonia catalyst of the type KATZ-55 (Fe promoted with alkali), ZnO, $3GeAs.Ge_2Se_3$, CaO, and a cracking aluminosilicate catalyst served as catalysts. A temperature rise in the volume was found for the Fe catalyst (Fig 1) and $3GeAs.Ge_2Se_3$ (Fig 4), which proved the course of reaction in the volume. This effect was distinctly marked in the case of Fe, whereas in the case of the semiconductor and ZnO it could be observed only at high temperatures. The thermocouple located in the reaction space showed no temperature rise for KATZ-55 (Fig 2), CaO, and the aluminosilicate catalyst (Fig 3), so that the reaction did not pass over into the volume when using these catalysts. The author thanks S.Z. Roginskiy, Corresponding Member of the AS USSR, for his helpful advice, and M.Ya. Kushnerov for his assistance in experiments. There are 4 figures and 6 references, 5 of which

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A Case of Homogeneous Continuation of a Heterogeneous Catalytic Reaction

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B004/B014

are Soviet.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR (Institute of Physical Chemistry of the Academy of Sciences, USSR)

PRESENTED: October 21, 1959, by P.A. Rebinder, Academician

SUBMITTED: October 8, 1959

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KRYLOV, O.V., YANOVSKIY, M.I. (DECEASED)

"Utersuchung akivierter Oberflachen einger Katalysatoren mit Hilfe von Isotpen-methoden."

Report presented at the 2nd Conf. on Stable Isotopes
East German Academy of Sciences, Inst. of Applied Physical Material
Leipzig, GDR 30 Oct - 4 Nov 1961

KRYLOV, O.V.

Possible causes of the nonhomogeneity of acid and basic catalysts-dielectrics. Kin.i kat. 2 no.5:674-678 S-O '61. (MIRA 14:10)

1. Institut khimicheskoy fiziki AN SSSR.
(Catalysts)

KRYLOV, O.V.; SINYAK, Yu.Ya.

New catalysts for the polymerization of ethylene oxide. Vysokom. soed. 3 no.6:898-900 Je '61. (MIRA 14:6)

1. Institut fizicheskoy khimii AN SSSR.
(Ethylene oxide) (Polymerization) (Catalysts)

S/076/61/035/003/019/023
B121/B206

5 1190 1209, 1274, also 1164

AUTHORS: Krylov, O. V. and Fokina, Ye. A.

TITLE: Catalytic properties of new semiconductors with the structure of zincblende

PERIODICAL: Zhurnal fizicheskoy khimii, v. 35, no. 3, 1961, 651-659

TEXT: The decomposition of isopropyl alcohol and hydrazine in the adsorption layer of the catalysts GaAs, Ga_2Se_3, $GaAs \cdot Ga_2Se_3$, $3GaAs \cdot Ga_2Se_3$, Ga_2Te_3, and CuBr was studied. These compounds of the types $A^{III}B^{V}$ and $A_2^{III}B_3^{VI}$ were prepared by N. A. Goryunova and placed at the authors' disposal. According to N. A. Goryunova, V. S. Grigor'yeva et al. (Ref. 13: Zh. tekhn. fiziki, 25, 1675, 1955), compounds of the $A_2^{III}B_3^{VI}$ type form solid solutions with compounds of the $A^{III}B^{V}$ type. The kinetic curves of the decomposition of isopropyl alcohol and hydrazine on these catalysts were recorded. From their course it may be seen that the decomposition of isopropyl alcohol at 130-270°C mainly proceeds in the form of dehydrogenation. The main decom-

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S/076/61/035/003/019/023
B121/B206

Catalytic properties ...

position products of hydrazine (90-250°C) are ammonia and nitrogen. The catalyst GaAs is not poisoned during the decomposition of isopropyl alcohol. The activation energy at temperatures below 220°C is ≈13-15 kcal/mole, and at temperatures above 225°C, ≈20-25 kcal/mole. The activation energy of the decomposition of N_2H_4 on GaAs at 100-200°C is approximately 16.5 kcal/mole. Besides dehydrogenation, other reactions occur on Ga_2Se_3. The activation energy of dehydrogenation amounts here to 14-19.5 kcal/mole. At 125-200°C, the decomposition of hydrazine on Ga_2Se_3 proceeds at a satisfactory rate. The decomposition of isopropyl alcohol on Ga_2Te_3 proceeds slowly at low temperatures, and 100% dehydrogenation sets in at elevated temperatures. A transition point lies at 145°C. At temperatures below 145°C, the activation energy of the decomposition of isopropyl alcohol is 2-3 kcal/mole, and at temperatures above 145°C, it is 11-19 kcal/mole. The decomposition of hydrazine on Ga_2Te_3 takes place at temperatures of 100-200°C. The catalytic activity of the compounds $GaAs \cdot Ga_2Se_3$ and $3GaAs \cdot Ga_2Se_3$ was only studied from the hydrazine decomposition, and it was established that the rate of reaction

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B121/B206

Catalytic properties ...

is slightly higher than on the catalysts GaAs and Ga_2Se_3. On CuBr, isopropyl alcohol decomposes at 200-270°C at a considerable rate. At 200°C, a 61% dehydrogenation takes place, and up to 270°C this proportion decreases to 36%. The activation energy of the reaction varies from 26 to 31 kcal/mole. Hydrazine on CuBr starts decomposing at 250°C, accompanied by side reactions and simultaneous chemical change of the catalyst under the formation of metallic copper. It was further established that in the series Ge, GeAs, ZnSe, CuBr and during the conversion of ZnTe to ZnSe and ZnS, and of Ga_2Te_3 to Ga_2Se_3, which groups of compounds show identical crystalline structure and similar lattice parameters, a decrease of the catalytic action sets in with simultaneous increase of the activation energy of the catalytic reaction, with an increase of the width of the forbidden band (i. e., with increasing ionic character of the bond). Semiconductors with bonds of highly ionic character have therefore poor catalytic properties. The authors thank S. Z. Roginskiy, Corresponding Member AS USSR, for advice. V. M. Frolov and Yu. N. Rufov are mentioned in connection with the study of the catalytic properties of pure germanium. There are 8 figures, 2 tables, and 19 references: 12 Soviet-bloc and 7 non-Soviet-bloc. The four most recent refer-

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ences to English-language publications read as follows: G. -M. Schwab, Semiconductors surface physics, Philadelphia, p. 283, 1957; G. -M. Schwab, Advances in Catalysis, N. Y., 9, 229, 1957; G. -M. Schwab, G. Greger, S. Krawczynski, J. Penzkofer, Z. phys. Chem. (N. F.), 15, 363, 1958; W. E. Garner, Advances in Catalysis, N. Y., 9, 169, 1957.

ASSOCIATION: Institut fizicheskoy khimii Akademiya nauk SSSR (Institute of Physical Chemistry of the Academy of Sciences USSR)

PRESENTED: May 19, 1959

SUBMITTED: July 15, 1959

GAZIYEV, G.A.; KRYLOV, O.V.; ROGINSKIY, S.Z.; SAMSONOV, G.V.; FOKINA, Ye.A.; YANOVSKIY, M.I.

Dehydrogenation of cyclohexane on certain carbides, borides, and silicides. Dokl. AN SSSR 140 no.4:863-866 O '61. (MIRA 14:9)

1. Chlen-korrespondent AN SSSR (for Roginskiy).
(Cyclohexane) (Dehydrogenation) (Catalysts)

S/204/62/002/005/002/007
E075/E136

AUTHORS: Krylov, O.V., and Sinyak, Yu.Ye.

TITLE: Catalysts for the polymerization of ethylene oxide

PERIODICAL: Neftekhimiya, v.2, no.5, 1962, 688-696

TEXT: The authors investigated the polymerization of ethylene oxide on several oxides and hydroxides of alkali-eurth metals to establish rules for the selection of effective catalysts. The materials examined were oxides, hydroxides and carbonates of Ca, Sr, Mg and Be, $Ba(OH)_2$, $CaSO_4$, $Ca(H_2PO_4)_2 \cdot H_2O$, CaF_2, $SrCl_2$, $BaCO_3$, $BaSO_4$, $Zn(OH)_2$, $ZnCO_3$, FeOOH, $Zr(OH)_4$, $Ni(OH)_2$, $Th(OH)_4$, $Co(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, silica gel, silica-alumina. Catalytic properties of NaCl, $(NH_4)_2CO_3$ and semiconductors ZnO, GaAs, etc., were investigated for purposes of comparison. The catalysts (0.2-0.5 g) were activated for purposes of 10^{-5} mm Hg) and then sealed in an ampule. A part of the ampule was filled with ethylene oxide (5 ml in 5 ml benzene) and separated from the catalyst by a glass partition. The polymerization started

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Catalysts for the polymerization... S/204/62/002/005/002/007
E075/E136

by breaking the partition. The most active hydroxide was $Be(OH)_2$ and BeO produced in the ampule by heating $Be(OH)_2$ under vacuum. At 90 °C BeO and $Be(OH)_2$ gave polymers having the molecular weight of 100 000 - 175 000, the rate of polymerization ranging from 1.3 to 6.2 millimoles/m^2.hours. $MgCO_3 \cdot Mg(OH)_2 \cdot H_2O$, MgO formed from $Mg(OH)_2$, $SrCO_3$ and CaO formed from $CaCO_3$ also had high activity at 90 °C, giving polymers having the molecular weight of 250 000, 350 000, 1 000 000, and 600 000 respectively, the rates of polymerization being 5.7, 1.45, 6.1 and 2.6 millimoles/m^2.hour respectively. Certain salts and hydroxides of Fe and Al also have high catalytic activity. In general the active compounds of transition metals have electronic configuration d_0 and d_8 (Fe^{3+}, Th^{4+}, Zr^{4+}, Ti^{4+}). The acidic catalysts (e.g. silica-alumina) were not active. The molecular weight M of the polymer increases as follows:

$$M = aV \frac{c_o - c}{S_1^o} \qquad (7)$$

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where: V - volume of ethylene oxide, mℓ; a - constant; c_0 and c - initial and final concentration of ethylene oxide respectively; S_1^0 - catalyst surface occupied by the active centres at t = 0. For $c_0 - c = \text{const}$, $\frac{1}{M}$ varies linearly with S_1^0. The apparent mean activation energies for the polymerization on various samples of $Be(OH)_2$, BeO and $BeO \cdot CO_2 \cdot 5H_2O$ ranged from 8.7 to 17 kcal. The reaction was most probably not diffusion controlled. The authors conclude that for the alkali-earth hydroxides at 90 °C the proportion of active centres decreases with the increasing atomic weight of the metal, but the activity of the individual centres tends to increase with the atomic weight. At 20 °C the order of the activities is reversed, since the energy of activation increases with the atomic weight of the metal. There are 3 figures and 6 tables.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR
(Institute of Chemical Physics, AS USSR)

SUBMITTED: May 5, 1962

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S/204/62/002/005/003/007
E075/E136

AUTHORS: Krylov, O.V., Kushnerev, M.Ya., and Fokina, Ye.A.

TITLE: Formation of active surface in the catalysts for the polymerization of ethylene oxide

PERIODICAL: Neftekhimiya, v.2, no.5, 1962, 697-704

TEXT: In view of the low activity of technical BeO and MgO, the authors studied the preparation of the active oxide catalysts by decomposing Be and Mg hydroxides and carbonates. The action of catalytic poisons (H_2O and CO_2) was also investigated. A MacBain balance was used to follow the decomposition and the adsorption kinetics of ethylene oxide (related to polymerization kinetics), CO_2 and H_2O. Adsorption of ethylene oxide occurs before polymerization, the rate of adsorption being proportional to log t (t = time). Subsequent polymerization takes place at a constant rate which depends on the number of active polymerization centres on the catalyst surface. The catalytic activity grows with the degree of decomposition of the hydroxides. The most active MgO has 30-50% of its surface covered by water. For $Be(OH)_2$ the most active catalyst results after its complete dehydration.

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Formation of active surface in the ... S/204/62/002/005/003/007
E075/E136

Freshly prepared MgO and BeO reduce their high activity on exposure to air, whilst their surface areas decrease by only 10-20%. This is explained by the preferential adsorption of water on the active centres, which lowers the adsorption and polymerization of ethylene oxide. Initial adsorption of CO_2 leads to the increase of ethylene oxide adsorption, but decreases the polymerization rate by a factor of 4-5. Further CO_2 adsorption has no effect. It is inferred from the adsorption kinetics that the active centres are Mg^{2+} or Be^{2+} ions interacting with the oxygen in ethylene oxide molecules.
There are 9 figures and 1 table.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR
(Institute of Chemical Physics, AS USSR)

SUBMITTED: May 5, 1962

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KRYLOV, O.V.

Data from the literature used for the selection of catalysts.
Kin.i kat. 3 no.4:502-508 Jl-Ag '62. (MIRA 15:8)

1. Institut khimicheskoy fiziki AN SSSR.
(Catalysts)

KRYLOV, O.V.; SINYAK, Yu.Ye.

Catalysts for ethylene oxide polymerization. Neftekhimiia 2 no.5: 688-696 S-O '62. (MIRA 16:1)

1. Institut khimicheskoy fiziki AN SSSR.
(Ethylene oxide) (Polymerization)
(Catalysts)

KRYLOV, O.V.; KUSHNEREV, M.Ya.; FOKINA, Ye.A.

Formation of the active surface of ethylene oxide polymerization catalysts. Neftekhimiia 2 no.5:697-704 S-O '62. (MIRA 16:1)

1. Institut khimicheskoy fiziki AN SSSR.
(Ethylene oxide) (Polymerization) (Catalysts)

KRYLOV, O.V.; MARKOVA, S.A.; FOKINA, Ye.A.; TRETYAKOV, I.I.

"Untersuching des Mechanismus der Adsorption und des Isotopenaustausches von CO2 an MgO und Mg(OH)2."

Third Working conference on Stable Isotopes, 28 October to 2 November 1963, Leipzig.

KRYLOV, O. V.; KUSHNEREV, M. Ya.; FOKINA, Ye. A.; MARKOVA, Z. A. 3

"Elementary mechanism of heterogeneous catalytic polymerization of ethylene oxide."

report submitted to 3rd Intl Cong on Catalysis, Amsterdam, 20-25 Jul 64.

(BR

ACCESSION NR: AP4035152 S/0195/64/005/002/0284/0292

AUTHOR: Kry*lov, O. V.; Fokina, Ye. A.

TITLE: Relationship between the catalytic activity of some semiconductors and the forbidden zone width

SOURCE: Kinetika i kataliz, v. 5, no. 2, 1964, 284-292

TOPIC TAGS: semiconductor catalysts, forbidden zone, forbidden zone width, catalysis, gadolinium semiconductor, germanium semiconductor, indium semiconductor, zinc semiconductor, copper semiconductor

ABSTRACT: Having found earlier that the catalytic activity of the isoelectronic series of germanium semiconductors (Ge, GaAs, ZnSe, CuBr) in the decomposition of isopropyl alcohol and hydrazine decreases from Ge to CuBr, the authors carried out a study to correlate the catalytic activity with the width of the forbidden zone. They studied decomposition of isopropyl alcohol in the adsorption layer (in steady-state conditions) at low pressure on the surface of the following semiconductors: BAs, BP, GaAs, GaAs·Ga_2Se_3 GaAs·$3Ga_2Se_3$, GaSb, , GaSe, GaTe, InAs, InSb, In_2Te_3 in the temperature interval of 50-320C. Over most of these semiconductors,

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ACCESSION NR: AP4035152

alcohol is dehydrogenated. The above data were compared with those obtained by the authors when decomposing alcohol over GdS, CuBr, Ga_2Se_3, Ga_2Te_3, Ge, ZnO, ZnS, ZnSe and ZnTe. It is shown that catalytic activity declines with the increasing width of the forbidden zone. With that, the decline of the rate constant may be caused by the decline of k_o rather than the increase in E. This fact may be explained by catalysis near the transition point from the impurity band to the conductivity band. It is shown in which cases the compensation effect is observed: symbatic change of E and log k_o. "Gratitude is expressed to S. Z. Roginskiy and V. M. Frolov for valuable discussions." Orig. art. has: 10 figures, 3 formulas, 1 table.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics AN SSSR)

SUBMITTED: 25Jul62 DATE ACQ: 20May64 ENCL: 00

SUB CODE: SS, GC NO REF SOV: 020 OTHER: 002

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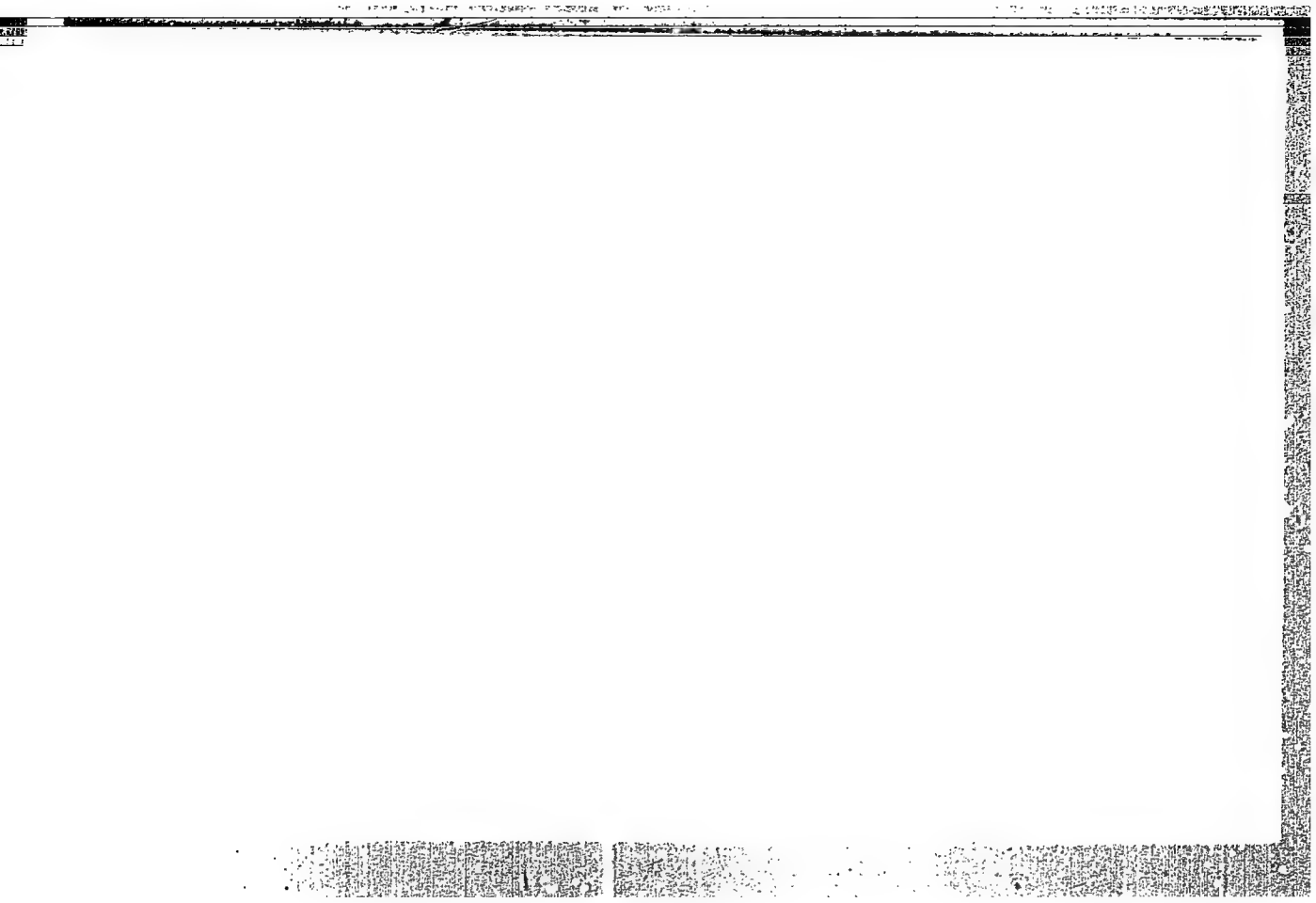

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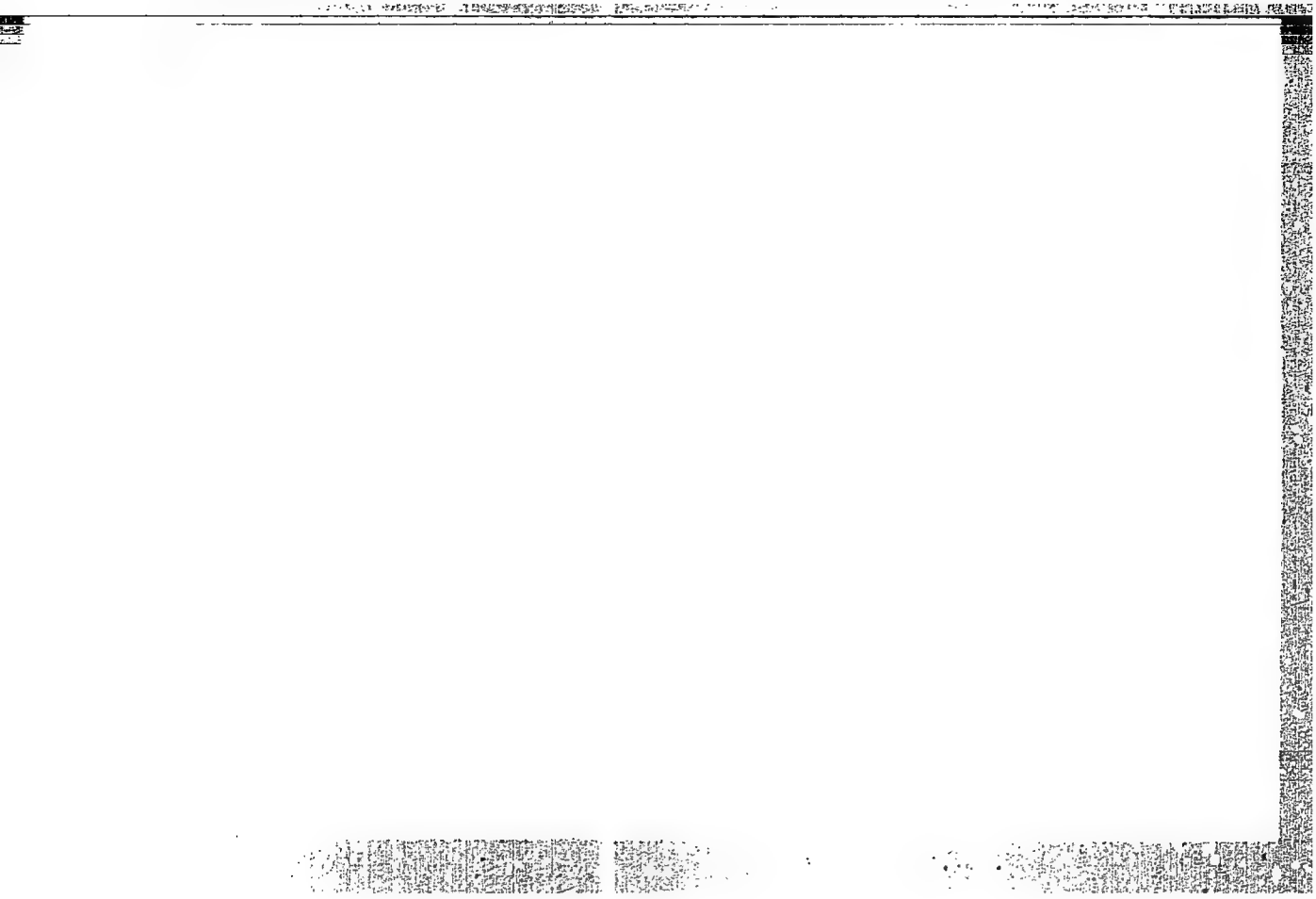

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KRYLOV, O.V.; MARKOVA, Z.A.; TRET'YAKOV, I.I.; FOKINA, Ye.A.

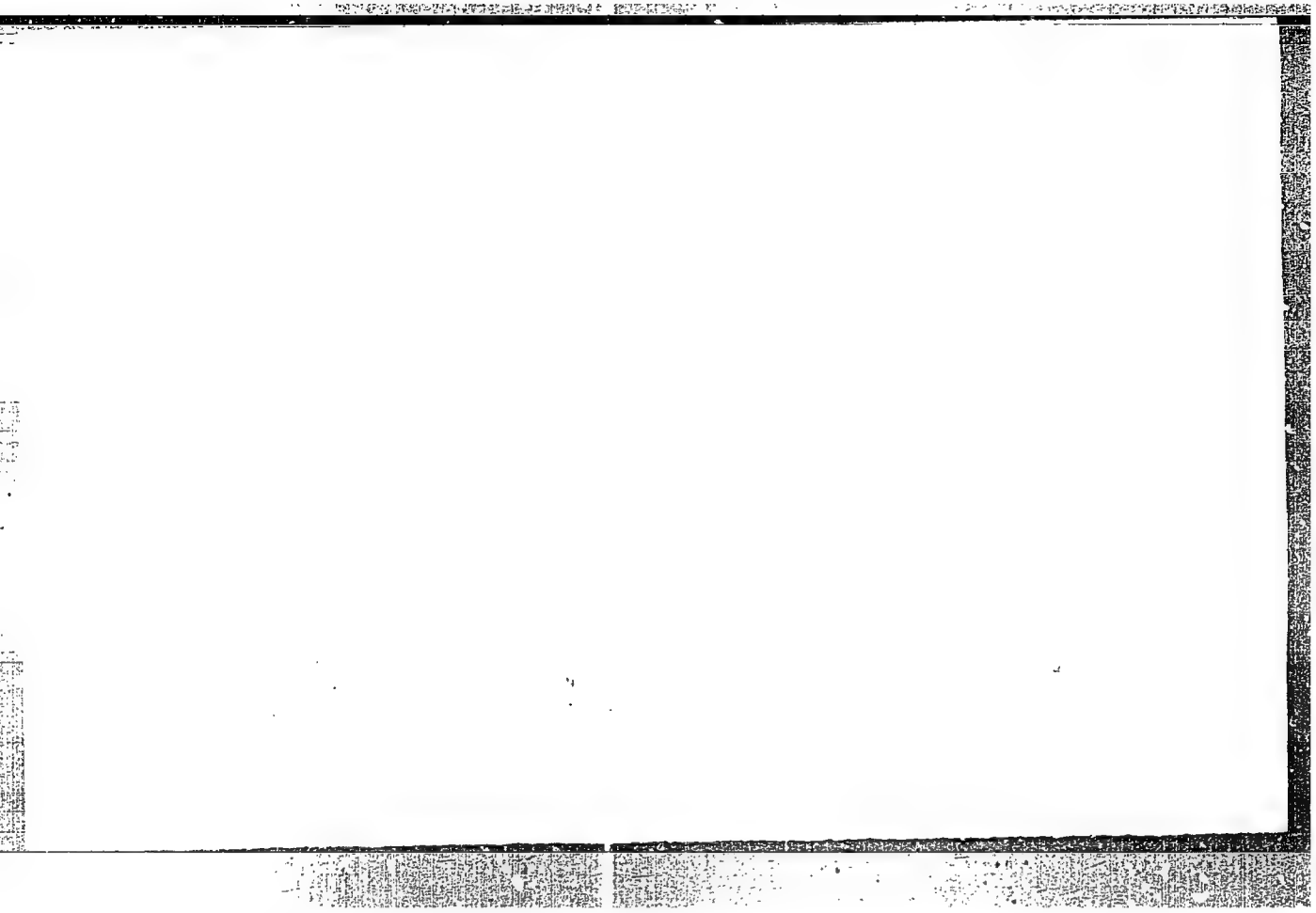
Mechanism of adsorption and isotope exchange of CO_2 on MgO and $Mg(OH)_2$. Kin. i kat. 6 no.1:128-136 Ja-F '65. (MIRA 18:6)

1. Institut khimicheskoy fiziki AN SSSR.

KRYLOV, O.V.; KUSHNEREV, M.Ya.; MARKOVA, Z.A.; ROZINA, Ye.A.

Mechanism of heterogeneous-catalytic polymerization of ethylene oxide. Vysokom. soed. 7 no.6:984-991 Je '65. (MIRA 18:9)

1. Institut khimicheskoy fiziki AN SSSR.



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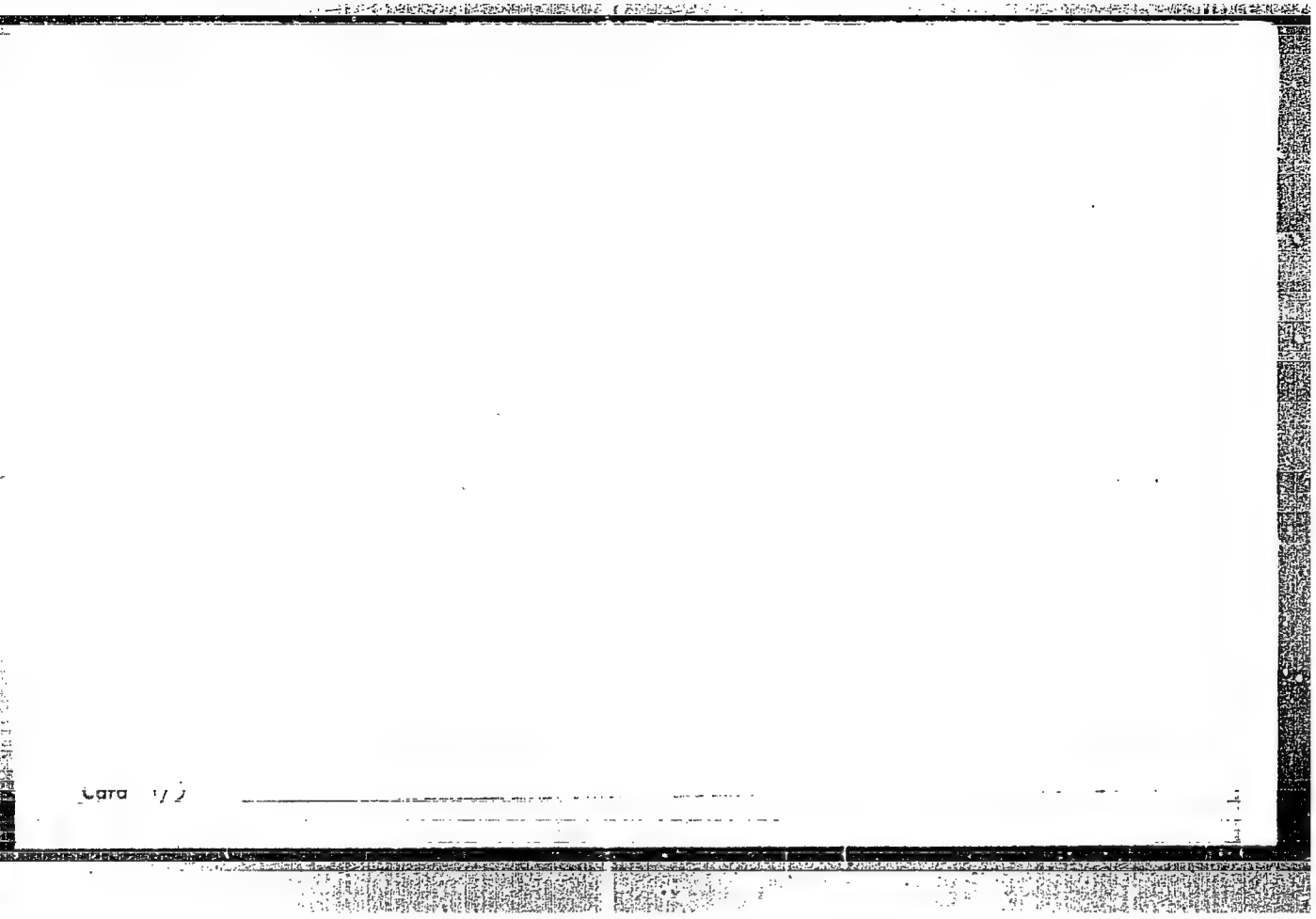

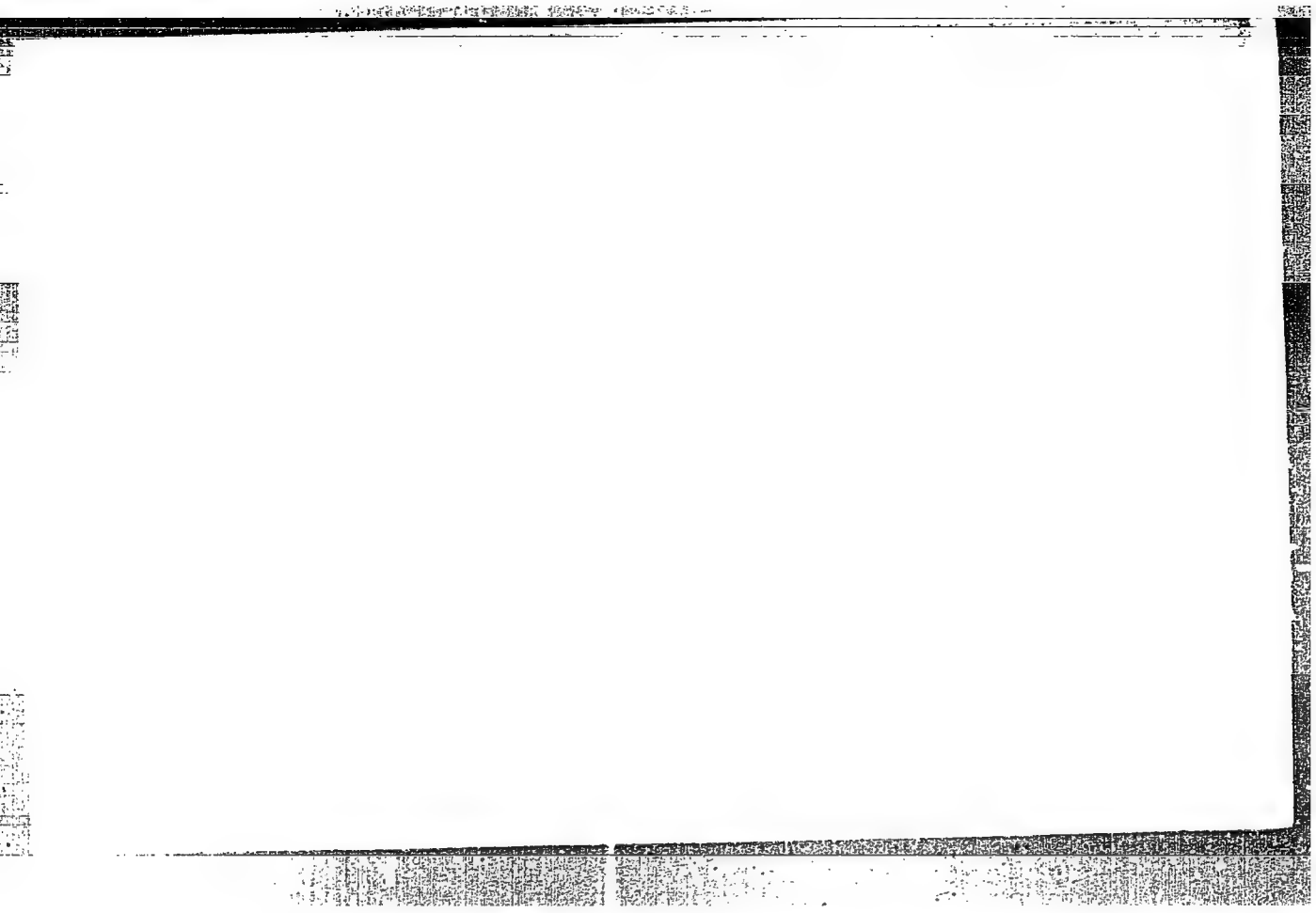

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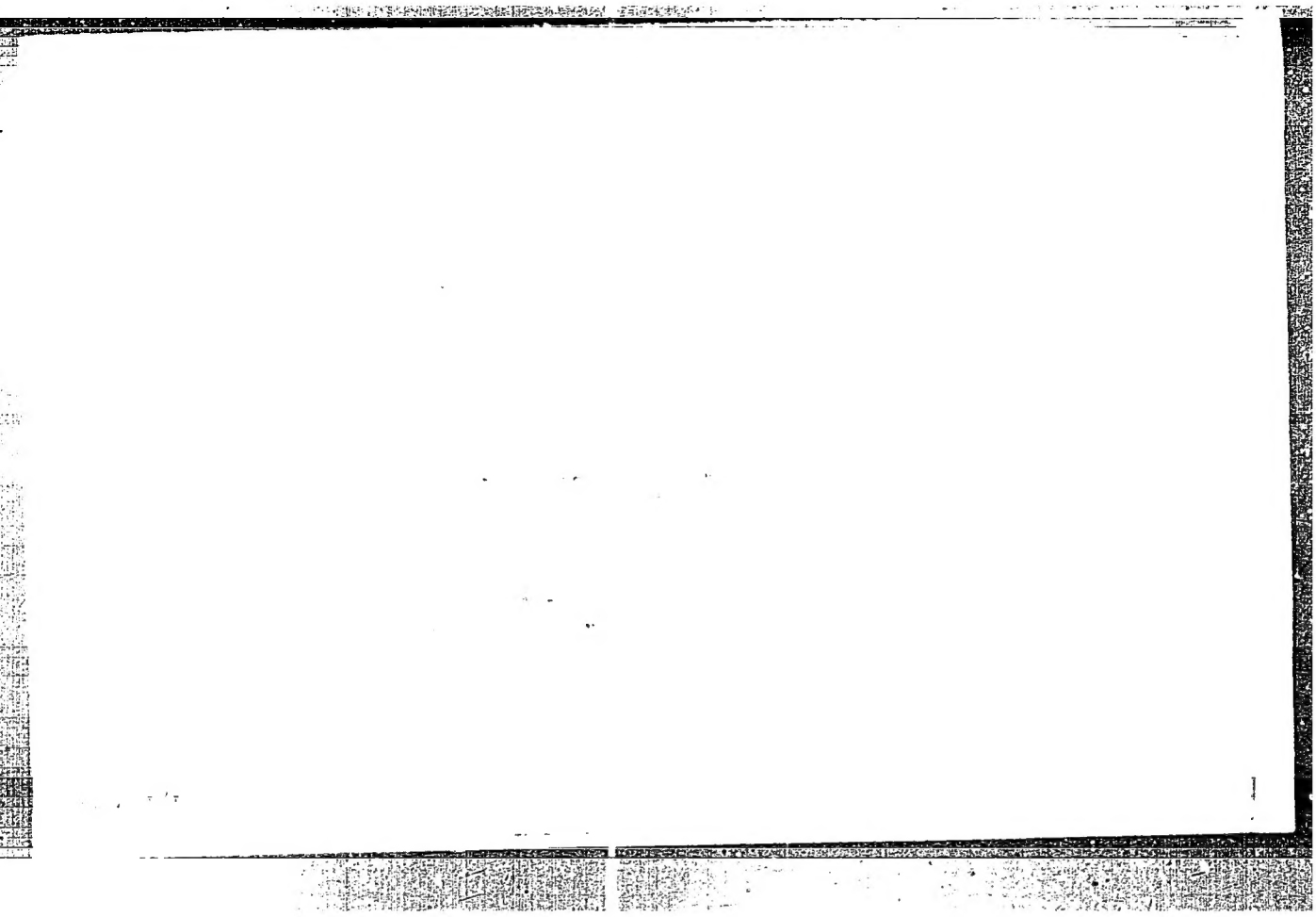

APPROVED FOR RELEASE: 06/14/2000 CIA-RDP86-00513R000826820020-3"

BARTAN, O.O.; KRYLOV, O.V.

New heterogeneous catalysts for polymerization of ethyleneimine.
Izv. AN SSSR. Ser. khim. no.11:2053-2054 '65.
(MIRA 18:11)

1. Institut khimicheskoy fiziki AN SSSR.

LIVSHITS, V.S.; KRYLOV, O.V.; KLABUNOVSKIY, Ye.I.

Heterogeneous catalytic polymerization of the optical isomers of propylene oxide. Dokl. AN SSSR 161 no.3:633-636 Mr '65.
(MIRA 18:4)

1. Institut khimicheskoy fiziki AN SSSR. Submitted September 5, 1964.

KRYLOV, O.V.

Mechanism of dehydration of alcohols. Zhur.fiz.khim. 39 no.11:2656-2663 N '65. (MIRA 18:12)

1. Institut khimicheskoy fiziki AN SSSR.